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Division of Chemical Science
(IZVESTIYA AKADEMII NAUK SSSR)
(Otdelenie Khimicheskikh Nauk)

IN ENGLISH TRANSLATION



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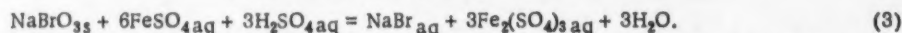
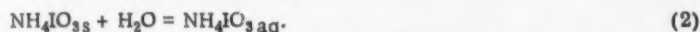
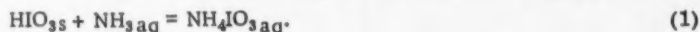
HEATS OF FORMATION OF AMMONIUM AND ALKALI-METAL HALATES

A. F. Kapustinskii, A. A. Shidlovskii, and Iu. S. Shidlovskaja

The available experimental data on the heats of formation of ammonium and alkali-metal halates are rather limited [1]. Kast [2] made the not altogether sound assumption that the ion-exchange reaction between solid salts $\text{NaClO}_3 + \text{NH}_4\text{Cl} = \text{NH}_4\text{ClO}_3 + \text{NaCl}$ proceeds without the evolution or absorption of heat and calculated that the heat of formation of ammonium chlorate is about 62.7 kcal/mole. The filling of this gap in thermochemistry is all the more interesting in view of the importance of some of these substances in pyrotechnics. We undertook measurements on NH_4IO_3 and NaBrO_3 with a view to the use of the results obtained in the estimation of some other constants which are at present unknown.

EXPERIMENTAL

In order to attain our object we carried out measurements at 25° on the heats of the following reactions:



Iodic acid of "Analytically Pure" grade was used; by neutralizing it with aqueous ammonia we obtained ammonium iodate. The ammonium iodate content of the dry preparation, determined iodometrically by the reaction $\text{IO}_3^- + 6\text{H}^+ + 5\text{I}^- = 3\text{H}_2\text{O} + 3\text{I}_2$ (the thiosulfate solution was standardized against "Chemically Pure" KIO_3), was found to be 99.9%. The sodium bromate content of our preparation, determined by the reaction $\text{BrO}_3^- + 6\text{H}^+ + 6\text{I}^- = 3\text{H}_2\text{O} + \text{Br}^- + 3\text{I}_2$, was found to be 98.5%. Aqueous ammonia and Mohr's salt ($\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$) of "Analytically Pure" grade were used; the sulfuric acid was "Chemically Pure".

The measurements were carried out in a calorimeter similar to that used by Kapustinskii and Iatsimirskii [3] for the determination of the heat of solution of sodium metaperiodate. The temperature was measured with the aid of a certificated calorimetric mercury thermometer reading from 23° to 27° in 0.01° divisions. The thermometer could be read within $\pm 0.001^\circ$. The water equivalent of the calorimeter was determined in an experiment on the dissolution of "Chemically Pure" KCl in water. In the calculations the heat of solution of KCl in 200 moles of water was taken to be 4.19 kcal/mole [4]. The rise or fall in temperature in our experiments was in the range 0.5-1.0°. When account is taken of the accuracy of measurement, the error of reading must be estimated as 0.2-0.4%. In none of the experiments did the duration of the main period exceed 6-8 minutes.

The results of the determinations are given in Table 1

CALCULATIONS AND DISCUSSION OF EXPERIMENTAL RESULTS

From the reported [1] data on the heats of formation ($-\Delta H_{298}$) of NH_3aq (19.32 kcal/mole) and HIO_3s (57.03 kcal/mole) and from the results of our measurements (Table 1 A and 1B), we find the value of the heat of formation of crystalline ammonium iodate:

$$-\Delta H_{298} = 19.32 + 57.03 + 10.0 + 7.6 = 94.0 \pm 0.2 \text{ kcal/mole}$$

From the reported [1] data on the heats of formation of NaBraq (10,000) (86.149 kcal/mole), H_2O (68.317 kcal/mole), $\text{Fe}_2(\text{SO}_4)_3\text{aq}$ (400) (653.0 kcal/mole), $\text{H}_2\text{SO}_4\text{aq}$ (600) (212.35 kcal/mole), and FeSO_4aq (200)

TABLE 1

Results of Calorimetric Experiments

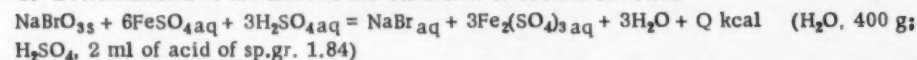
A. Determination of the Heat of Solution of NH_4IO_3 in H_2O

Amount of NH_4IO_3 (g)	Dilution	Change in temperature with correction for radiation ($^{\circ}\text{C}$)	Including radiation correction ($^{\circ}\text{C}$) of	Water equivalent of calorimeter (cal)	Heat of solution per mole of salt (kcal)	Mean heat (kcal/ mole)
5.428	800	- 0.494	0.009	435	- 7.64	- 7.6
5.397	807	- 0.489	0.017	435	- 7.60	
5.430	800	- 0.484	0.014	435	- 7.48	

B. Determination of the Heat of Neutralization $\text{NH}_3\text{aq} + \text{HIO}_3\text{s} = \text{NH}_4\text{IO}_3\text{aq} + \text{Q kcal}$ (0.1 N)

Amount of HIO_3 (g)	Dilution of resulting NH_4IO_3	Change in temperature with correction for radiation ($^{\circ}\text{C}$)	Including radiation correction ($^{\circ}\text{C}$) of	Water equivalent of calorimeter (cal)	Heat of reaction according to equation (kcal)	Mean heat (kcal)
5.574	730	+ 0.730	0.025	435	+ 10.00	+ 10.0
4.940	818	+ 0.641	0.016	435	+ 9.94	
5.375	755	+ 0.697	0.014	435	+ 9.93	

C. Determination of the Heat of the Oxidation-Reduction Reaction



Amount of NaBrO_3 (g)	Amount* of Mohr's salt (g)	Rise of temperature ($^{\circ}\text{C}$)	Including radiation correction ($^{\circ}\text{C}$) of	Water equivalent of calorimeter (cal)	Heat evolved (cal)	Heat of reaction according to equation (kcal)
0.337	6.0	0.625	0.012	422	263.7	118.1
0.338	6.0	0.626	0.039	422	264.2	117.9
0.332	6.0	0.622	0.003	422	262.4	119.3

Mean 118.4 kcal

* Mohr's salt was taken in excess over the stoichiometric amount; for 0.34 g of NaBrO_3 5.3 g of Mohr's salt is theoretically required.

(236.0 kcal/ mole) and from the results of our measurements (Table 1C), we find the value of the heat of formation of crystalline sodium bromate:

$$-\Delta H_{298} = 86.149 + 68.317 \cdot 3 + 653.0 \cdot 3 - 212.35 \cdot 3 - 236.0 \cdot 6 - (118.4 \cdot 100 : 98.5) = 76.8 \pm 0.5 \text{ kcal/ mole.}$$

In conjunction with the already known thermochemical constants of halates, this enables us to estimate theoretically the heats of formation of certain compounds by the method of constant differences.

The empirical establishment of the constancy of differences between heats of formation of compounds of a given type is to be traced back to the work of Favre and Silberman [5] and, particularly, Thomsen [6]. This generalization, which Luginin [7] called the law of constant differences, was at first regarded as an empirical rule, but Kablukov [8] succeeded in proving that it is closely associated with Arrhenius's theory of electrolytic dissociation.

Finally, Kapustinskii [9] showed in a more rigorous manner that this law is applicable to dilute solutions of strong electrolytes, from the properties of which it follows quite strictly and for which it can be given the following formulation, which is exact and has no exceptions: for strong electrolytes at infinite dilution, the differences in heats of formation of electrolytes having a common ion do not depend on the nature of the common ion, but are equal to the differences in the heats of formation of the noncommon ions, and are therefore constant.

TABLE 2

Calculation of Unknown Heats of Formation of Crystalline Ammonium Salts (per mole)

A. Constant difference $K^+ - NH_4^+ = 28.4 \text{ kcal/g-equiv.}$

Anion	ΔH_{298} of potassium salt (kcal) [1]	Calculated $-\Delta H_{298}$ of ammonium salt (kcal)
ClO_3^-	93.5	65 ± 2
BrO_3^-	79.4	51 ± 2
IO_3^-	121.5	93 ± 2
MnO_4^-	194.4	166 ± 2

B. Constant difference $Na^+ - NH_4^+ = 22.6 \text{ kcal/g-equiv}$

Anion	$-\Delta H_{298}$ of sodium salt (kcal)	Calculated $-\Delta H_{298}$ of ammonium salt (kcal)
IO_4^-	104.0 [3]	81 ± 1.5
SeO_4^{2-}	258 [1]	213 ± 3

The limits of applicability of this law, as also its content, are expressed quite clearly; it is however tempting to try to extend it, even as an approximation, not only to the thermochemistry of solutions, but also to heats of formation in general, including those of solid compounds. This has been done for a long time by various authors. Thus, the linearity of the relation between heats of formation of two series of compounds having a common ion was shown in graphical form by Kapustinskii and Samoilov [10] for metal oxalates and carbonates in 1950. We decided to verify the constancy of the difference in heats of formation of solid salts having a common anion for the cases of interest to us: potassium, sodium, and ammonium salts.

From a comparison of the heats of formation of twenty pairs of crystalline potassium and ammonium salts we concluded that the heat of formation of potassium salts exceeds that of ammonium salts having the same anion by $28.4 \pm 2 \text{ kcal/g-equiv.}$ Thus, the heat of formation of KCl is $104.2 \text{ kcal/g-equiv.}$ and that of NH_4Cl is $75.4 \text{ kcal/g-equiv.}$ the difference $K^+ - NH_4^+$ is $104.2 - 75.4 = 28.8 \text{ kcal/g-equiv.}$ Departures from the average difference of more than $\pm 2 \text{ kcal}$ occur comparatively rarely.

By an analogous comparison of heats of formation for twenty pairs of crystalline sodium and ammonium salts we found the difference

$$Na^+ - NH_4^+ = 22.6 \pm 1.5 \text{ kcal/g-equiv.}$$

This departure ($1.5\text{-}2 \text{ kcal/g-equiv.}$) is 7% of the mean difference and not more than 1.5-2% of the heat of formation of 1 g-equiv of salt.

Using these values of the differences, we may calculate, without any pretensions to high accuracy, the heats of formation of certain ammonium salts that are difficult to investigate experimentally (Table 2).

For ammonium iodate the calculated heat of formation (93 kcal/mole) is identical with the value we found by experiment (94.0 kcal/mole) within the limits of accuracy ($\pm 2 \text{ kcal/mole}$) indicated in Table 2.

By the use of the above difference values the heat of formation of sodium bromate may also be calculated.

* The following are exceptions: HS^- , HSO_4^- , CNO^- , $CH_3CO_2^-$; but even for these the departure from the mean difference does not exceed 4 kcal/g-equiv.

The difference $K^* - Na^* = (K^* - NH_4^*) - (Na^* - NH_4^*)$, and we obtain $28.4 - 22.6 = 5.8$ kcal/mole. In thermochemical reference books Rossini, Wagman, and others give 79.4 kcal/mole for $KBrO_3$, and Britske, Kapustinskii, and others give 81.6 kcal/mole. For $NaBrO_3$, therefore, we can calculate two possible values, which differ by almost 2 kcal: $79.4 - 5.8 = 73.6$ kcal/mole and $81.6 - 5.8 = 75.8$ kcal/mole. The value of 76.8 kcal/mole, which we obtained from $NaBrO_3$, agrees satisfactorily with the calculated value.

SUMMARY

1. Standard heats of formation of ammonium iodate and sodium bromate were determined by the calorimetric method: NH_4IO_3 (crystalline), $\Delta H_{298} = -94.0 \pm 0.2$ kcal/mole; $NaBrO_3$ (crystalline), $\Delta H_{298} = -76.8 \pm 0.5$ kcal/mole.

2. The unknown heats of formation of various ammonium salts (halates and others) for which experimental investigation is difficult were calculated by the method of constant differences.

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ADSORPTION OF NITROGEN VAPOR ON GRAPHITIZED CARBONS AND CHARCOAL

A. V. Kiselev and E. V. Khrapova

It has been pointed out [1-4] that it is preferable to work with carbon blacks rather than with active charcoals and graphites (low porosity with large surface). The heterogeneity and roughness of the surfaces of carbons can be considerably reduced by heating them at high temperatures; the crystallites in the carbon particles then increase in size, and they change in shape from spherical to polyhedral [5-7]. The surfaces of carbon blacks become more homogeneous and their properties approach those of a graphite surface [3, 5-10]. We have carried out a series of investigations on the adsorption and differential heats of adsorption of various vapors on carbons [1-4, 10-17] and on adsorption from solutions [18, 19].

The adsorption isotherms of nitrogen vapor on carbons are usually used only for the determination of the specific surface s [20]. In such work the effect of the nature and structure of the adsorbent surface on the adsorption of nitrogen is not considered, though it is very important to know the extent to which the adsorption of a substance used for the determination of surface area depends on its structure. The detailed study of the adsorption of substances such as nitrogen and the inert gases is also of interest for its own sake, for their adsorption properties toward graphite can be calculated theoretically with comparative ease [21-25].

Adsorption isotherms for nitrogen and inert-gas vapors in the uni-molecular region have received scarcely any study. Some investigations [8, 9, 26-28] have been carried out on the heat of adsorption for coverages θ ranging from 0.3 to 0.5 and higher, but the adsorption isotherms are given for a still narrower range. Only in two investigations [24, 29] have the adsorption isotherms of nitrogen, argon, and krypton vapors been studied at coverages ranging up from about 0.02 (on P-33 carbon graphitized at 2700°). In the multimolecular region the adsorption isotherms of the vapors of nitrogen and argon [5] and of krypton [26] have been determined on the same carbon.

In the present work we have investigated the adsorption of nitrogen vapor on various samples of original and graphitized carbons and active charcoal at coverages ranging from very low values. The results are compared with data in the literature for the adsorption of nitrogen, argon, krypton, and methane vapors.

EXPERIMENTAL

The following original samples were taken for investigation: two channel carbon blacks, namely Spheron 6 degassed at 900° [14] and Ukhtinsk carbon degassed at 800° [18]*, and a homogenous finely porous charcoal [4] degassed at 800°. All these samples, and also carbon P-33 investigated previously [15], were then roasted at 1700°** in a stream of hydrogen for 90 minutes as in a previous investigation [3] and were subjected to prolonged degassing at 280°, until the pressure was less than 10^{-6} mm, before being used in the experiments.

The original Ukhtinsk carbon contained 1% by weight of oxygen and 0.5% of hydrogen; it had acidic properties; the adsorption of alkali was 0.2 mg-equiv/g (according to Kovaleva's results).

The adsorption isotherms were determined in the volumetric gas apparatus constructed by Dreving and used in previous investigations [14, 30]. It consisted of ampoules containing adsorbent, a McLeod gage for measuring

*It has been shown [6, 7] that appreciable graphitization of carbon begins at 1000°.

**It has been shown [6] that roasting of carbons at 1700-2000° results in a sharp increase in the degree of graphitization, as determined by the reduction in the distance along the c axis between planes of the crystallites of the carbon, whereas with further rise in temperature the degree of graphitization changes very little.

pressures up to 3.85 mm, a U-tube manometer, a gas cylinder and gas buret, and a tube, diameter 3 mm, connecting them to the adsorption ampoule. The components concerned with the measurement were contained in a thermostat

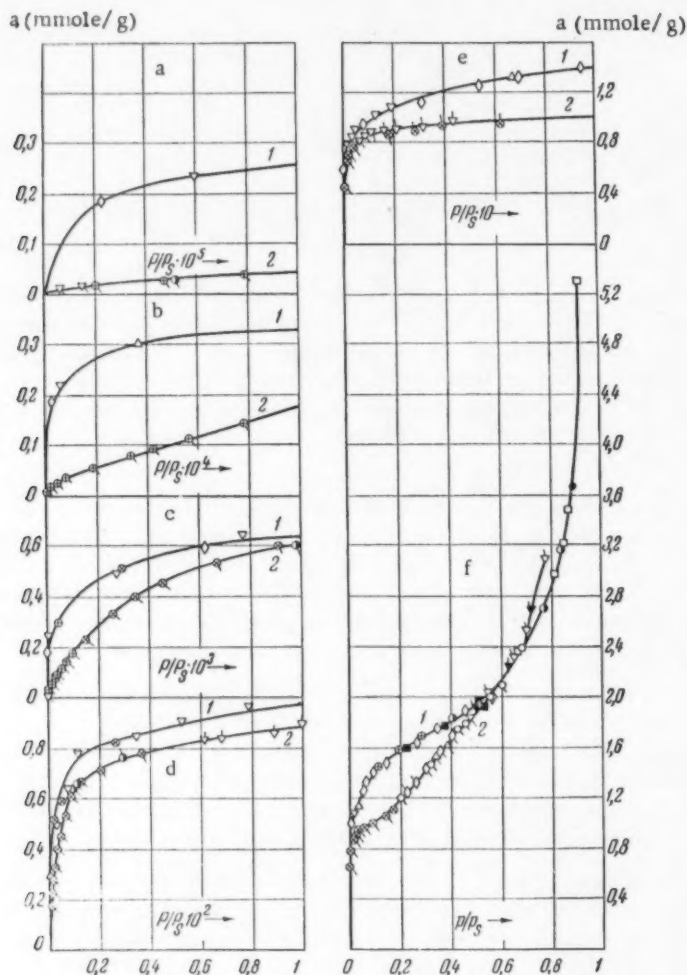


Fig. 1. Adsorption isotherms of nitrogen vapor at -195° on 1) original channel carbon black Spheron 6 (900°) and 2) graphitized Spheron 6 (1700°). Here and in later graphs the different markers for the points refer to different series of experiments; the black markers refer to desorption.

($\pm 0.1^{\circ}$), and the adsorption ampoule was in a Dewar vessel containing technical liquid nitrogen. In order to reduce the error made in the determination of the volume of the cooled part of the ampoule resulting from changes in the level of the liquid nitrogen, the connecting tube was contained in an evacuated jacket. The pressure of saturated nitrogen vapor p_s corresponding to the temperature in the Dewar vessel was determined with a nitrogen thermometer. The relative error in the adsorption determination for samples of the smallest surface area in the p/p_s range from 10^{-4} to 0.1 did not exceed 0.6%, and for $p/p_s > 0.6$ it did not exceed 1%. The maximum error was at $p/p_s > 10^{-5}$, but even then it did not exceed 3-5%. At low pressures corrections were made for the thermomolecular effect [31], and at high pressures corrections were made for the departure from the law of ideal gases [32]. The U-manometer was read accurately within 0.01 mm with a KM-10 cathetometer. Nitrogen was purified by passage through soda-lime, silica gel cooled with liquid nitrogen, heated copper catalyst, and a trap cooled with liquid nitrogen.

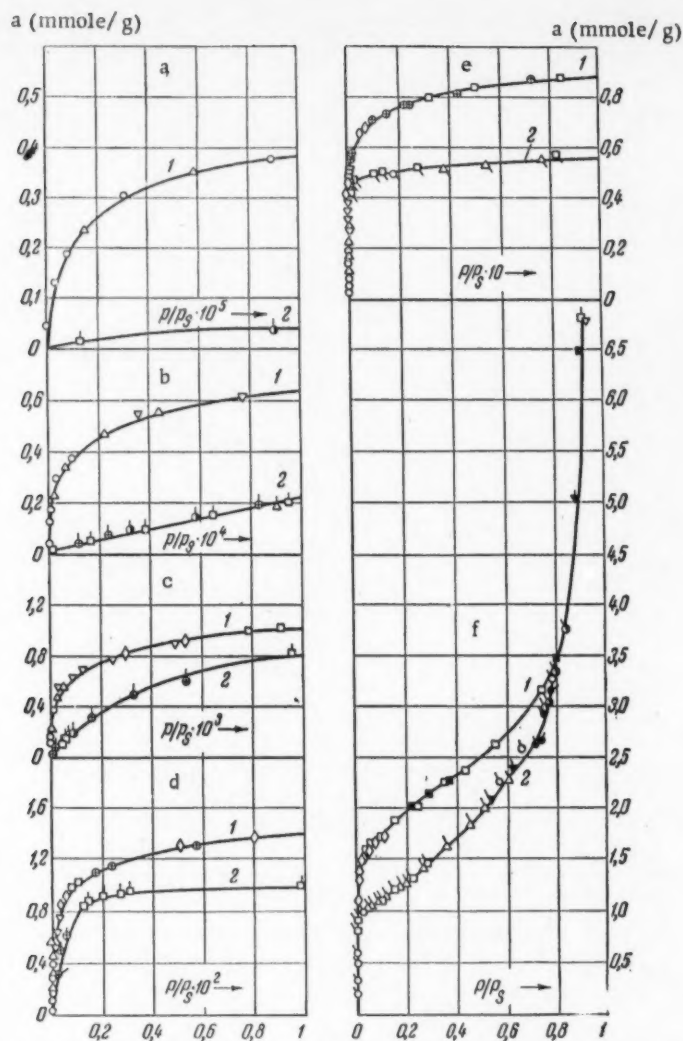


Fig. 2. Adsorption isotherms of nitrogen vapor at -195° on
1) original and 2) graphitized Ukhinsk channel carbon black.

Relative Adsorption (per gram of adsorbent)

Carbon Blacks. Figures 1 and 2 give adsorption isotherms of nitrogen vapor at -195° on original and graphitized Spheron 6 and Ukhinsk channel carbon blacks expressed on six different scales. As can be seen from Figures 1 and 2, the thermal treatment of the carbons sharply reduced the adsorption per unit weight; over the whole p/p_s range investigated adsorption on graphitized carbons is lower than on the original carbons. For p/p_s values ranging from $1 \cdot 10^{-5}$ to $1 \cdot 10^{-4}$ (Figures 1b and 2b) the isotherms for graphitized carbons are very nearly linear. After the completion of a monolayer (Figures 1f and 2f) the adsorption isotherms for graphitized carbons become wavelike in form.* The adsorption isotherm for the graphitized carbon P-33 was studied at p/p_s values ranging from 10^{-6} to 0.9. There was again a linear section in the p/p_s range from $2 \cdot 10^{-6}$ to $1.8 \cdot 10^{-5}$, beyond which the isotherm became curved. At higher p/p_s values waves appeared on the isotherm, and these were more marked than in the case of the graphitized channel carbons (see below).

*It has been found [14] that Spheron 6 carbon that had been "defrosted" after removal of liquid nitrogen showed enhanced adsorption. For the other carbons that we studied, and also for graphitized Spheron 6, no such effect was observed.

Charcoal. Figure 3 gives adsorption isotherms of nitrogen vapor at -195° on original and graphitized finely porous charcoal. Here, as in the case of other vapors [4], graphitization results in a sharp reduction in adsorption.

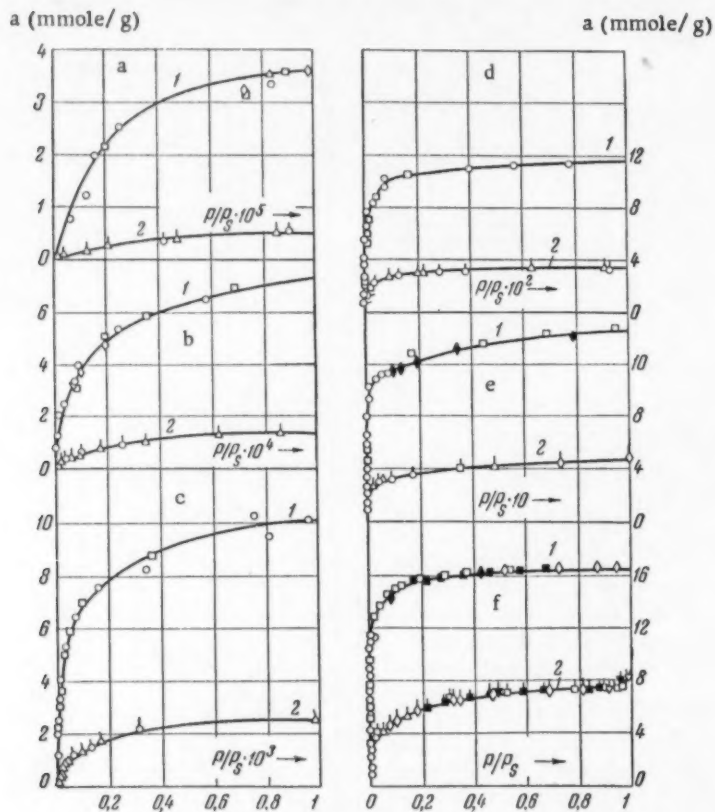


Fig. 3. Adsorption isotherms of nitrogen vapor at -195° on 1) original and 2) graphitized [2] homogeneously and finely porous charcoal.

The volume V_s of liquid nitrogen adsorbed at saturation, which expresses the volume of pores, diminishes from 0.57 to 0.25 cc/g, i.e., by more than one-half. The reduction in the steepness of the isotherm in the initial region and its S-form near saturation in the case of the graphitized sample indicates the destruction of some of the fine pores during graphitization on account of crystallite growth.

Equations of Adsorption Isotherms

The appearance of linear sections on the isotherms at low p/p_s and waves in the multimolecular region [5, 26, 33-37] indicates that the roasting of carbons makes their surfaces considerably more homogeneous. This is shown clearly by measurements of heats of adsorption [3, 7-9, 26-28].

The Langmuir and BET equations were applied to the isotherms obtained.* The results are given in the table, and Fig. 4 gives an example for graphitized Spheron 6. The adsorption isotherms of unroasted samples do not follow the Langmuir isotherm.

It will be seen from Fig. 4 and the table that for graphitized samples the Langmuir equation is applicable over

* The initial concave part of the adsorption isotherm of nitrogen vapor on carbon P-33 graphitized at 2700°C is described by Hill's equation [24]. In a future communication we shall examine the description of adsorption isotherms of nitrogen vapor over a wide range of coverages by a single more complete equation [38].

a considerable range of p/p_s values and θ , so that the applicability of the BET equation is extended toward the lower values of p/p_s . The values of the volume of a monolayer a_m obtained for these samples from the two equations

TABLE

Change in the Specific Surfaces of Carbons and Charcoal During Graphitization, and the Limits of Applicability of Adsorption-Isotherm Equations for Nitrogen Vapor

Sample	Original			Graphitized				
	BET equation			Langmuir equation		BET equation		
	a_m (m-moles/g)	$\frac{s}{(sq.m/g)}$	p/p_s range	a_m (m-moles/g)	p/p_s range	a_m (m-moles/g)	$\frac{s}{(sq.m/g)}$	p/p_s range
Ukhtinsk carbon	1.56	152	from $2 \cdot 10^{-3}$ to 0.2	1.03	from $2 \cdot 10^{-4}$ to $8 \cdot 10^{-2}$	1.04	100	from $2 \cdot 10^{-4}$ to 0.2
Spheron 6 carbon	1.28	125[14]	from 0.01 to 0.2	0.94	from $2 \cdot 10^{-4}$ to $6 \cdot 10^{-2}$	0.94	92	from $2 \cdot 10^{-4}$ to 0.2
P-33 carbon	0.163	15.9[15]		0.140	from $1 \cdot 10^{-4}$ to $8 \cdot 10^{-2}$	0.137	13.4	from $1 \cdot 10^{-4}$ to 0.2
Finely porous charcoal	12.3	(1150)	from 0.01 to 0.2	—	—	4.61	(450)	from 0.01 to 0.2

are very close. All this indicates the homogeneity of the surface of graphitized carbons. Interaction between adsorbate molecules [24, 29, 38], although present, is small in comparison with the energy of interaction between adsorbate and adsorbent; this view is supported by calorimetric data [9, 26, 27].*

The assumption that adsorption has the same character in the second and subsequent layers, which lies at the basis of the BET equation, leads to departures from this equation at high p/p_s values [3]. The equation of Halsey [37] and Hill [39], which takes approximate account of differences in adsorption in layers of differing thickness in the multimolecular region, is inapplicable in the case of the original carbons; for graphitized carbons it is valid in the p/p_s range 0.1-0.5 when the power index n is given the value of 1.65-1.75.

The specific surfaces s of the samples studied were calculated from the BET equation. The area occupied by a nitrogen molecule in a compact monolayer was taken to be 16.2 \AA^2 . In all cases s was reduced by graphitization. Owing to the great roughness of the original carbons, the values of s determined with the BET equation from the adsorption isotherms of nitrogen vapor have a somewhat conditional significance. In the case of the adsorption of nitrogen vapor on charcoals, the BET equation is valid in a purely formal way. In fact, a_m for graphitized finely porous charcoal is 60% of the limiting value a_s , i.e., as in the case of the adsorption of hydrocarbons [40, 41], it is clearly too high. Hence, specific surfaces of charcoals calculated from the BET equation cannot be regarded as trustworthy. Since "absolute" isotherms obtained in this way for carbons and charcoals coincide in the range 0.1-0.2, they can be considered to take up a reduced form at, e.g., $p/p_s = 0.2$ [42].

Absolute Isotherms (for unit surface of adsorbent)

Effect of Graphitization of Carbon Black. In the elucidation of the adsorption properties of carbons it was of interest to compare values of adsorption for original and graphitized samples referred to unit surface. Fig. 5 represents adsorption isotherms of nitrogen vapor on original and graphitized Spheron 6 channel carbon referred

*Similar behavior is observed in the adsorption of hydrocarbons [3, 10, 16].

to unit surface, as determined by the BET equation. A noteworthy feature is the sharp difference in the initial parts of the isotherms (Figures 5a and 5b). In this region the adsorption isotherm for the original carbon rises steeply

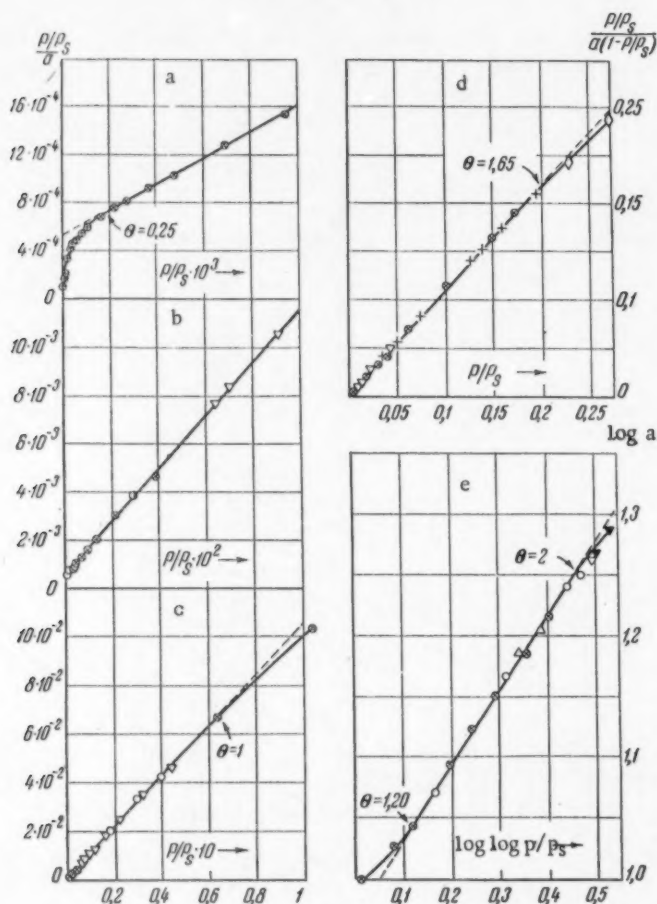


Fig. 4. Left: adsorption isotherm of nitrogen vapor at -195° on Spheron 6 carbon graphitized at 1700° in the coordinates of the Langmuir equation (a, b, and c). Right: the same isotherm in the coordinates of the BET equation (d) and of the Halsey and Hill equation (e). The crosses represent the results of N. N. Avgul', obtained with another apparatus. Values of θ are indicated by arrows.

and is highly curved, whereas that for the graphitized carbon rises much more slowly. However, even in the case of the graphitized carbon the initial part of the isotherm is not linear, probably because there is still some residual roughness [3, 9, 27]; it is linear in the p/p_s range from $1 \cdot 10^{-5}$ to $1 \cdot 10^{-4}$. The sharp change in the form of the initial sections of the adsorption isotherms of nitrogen vapor in passage from the original sample to the graphitized sample, and also the corresponding reduction in specific surface from 125 to 92 sq.m/g, indicates reduction in the surface roughness.* At $p/p_s = 4 \cdot 10^{-4}$, $\theta = 0.55$ (Fig. 5c); the isotherms intersect, but again approach one another

*The roughness of the original samples is associated with the disordered distribution within their particles of nuclei, i.e., graphite crystallites covered (particularly over the prismatic faces) with an encrustation of chemical compounds containing carbon, oxygen, and hydrogen; it is associated also with the formation of fissures and depressions as these compounds are gradually removed during heating in a vacuum at temperatures of up to 900° . The thermal treatment of carbons above 1000° , which brings about considerable growth and orientation of the graphite crystallites, results in the smoothing of the adsorbing surface.

at $\theta \approx 1$; the adsorption isotherm for the original carbon then takes the lower place. The causes of such changes in the form of the adsorption isotherm on graphitization of the carbon lie both in reduction of surface roughness and in the destruction of surface compounds.

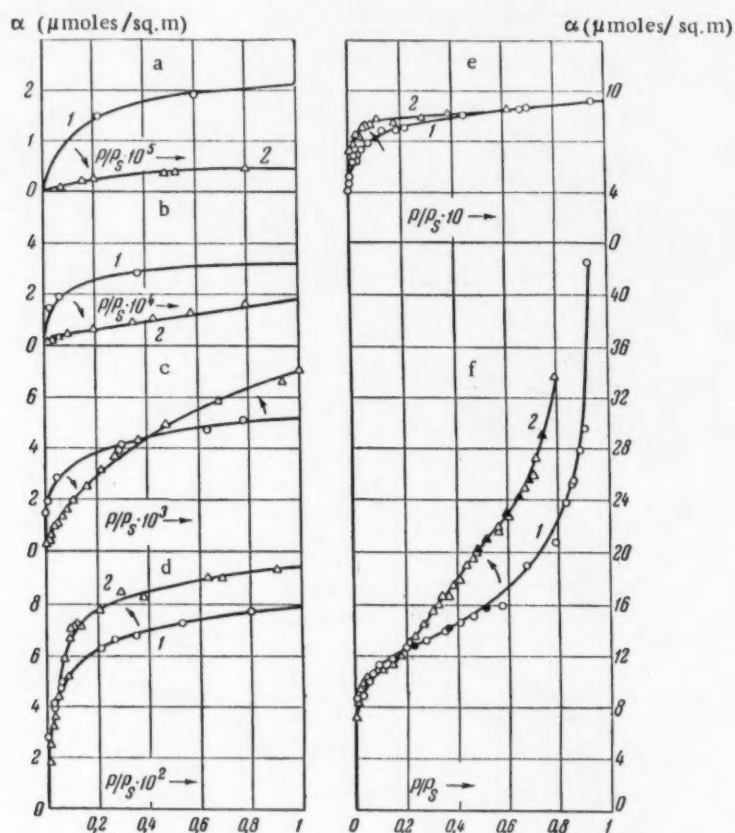


Fig. 5. Absolute adsorption isotherms of nitrogen vapor at -195°C on 1) original (900°C) and 2) graphitized (1700°C) Spheron 6 channel carbon. The arrows indicate the direction of change in the isotherms on passage from the original sample to the graphitized sample.

The elucidation of the effect of the geometric factor (roughness) is aided by comparison of adsorption isotherms of nitrogen vapor on graphitized samples of carbon and charcoal for which differences in the chemical state of the surface are small. Such a comparison is made in Fig. 6. As we pass from carbon to charcoal at low p/p_s values, the steepness of the isotherm increases sharply. However, further increase in p/p_s slows down the rise of the isotherm for adsorption on charcoal, so that the isotherms intersect at $p/p_s \approx 5 \cdot 10^{-4}$; subsequently, owing to the filling of the fine pores of the charcoal with adsorbed nitrogen, the charcoal adsorption isotherm goes considerably below the carbon black isotherm. Comparison of Figures 6 and 5 reveals a certain analogy in the change in the form of the isotherms as we pass from the original to the graphitized carbon (Fig. 5) with the corresponding change as we pass from charcoal to graphitized carbon (Fig. 6). This indicates the importance of the geometric factor (reduction in the roughness of the carbon surface in the graphitization), particularly in the initial region of coverage. This lowering of the absolute adsorption isotherm of nitrogen vapor on the original sample at $\theta > 1$ may also be associated with the effect of roughness, namely with the complete filling of cavities in the roughest part of the surface with reduction in the area of the adsorbed film on which adsorption proceeds in the multimolecular region.

The change in the form of the adsorption isotherm of nitrogen vapor in the graphitization of the carbon is affected also by chemical and crystallochemical factors: destruction of surface compounds, and growth and orientation of graphite crystallites. These factors are probably most in evidence in the covering of the less rough part

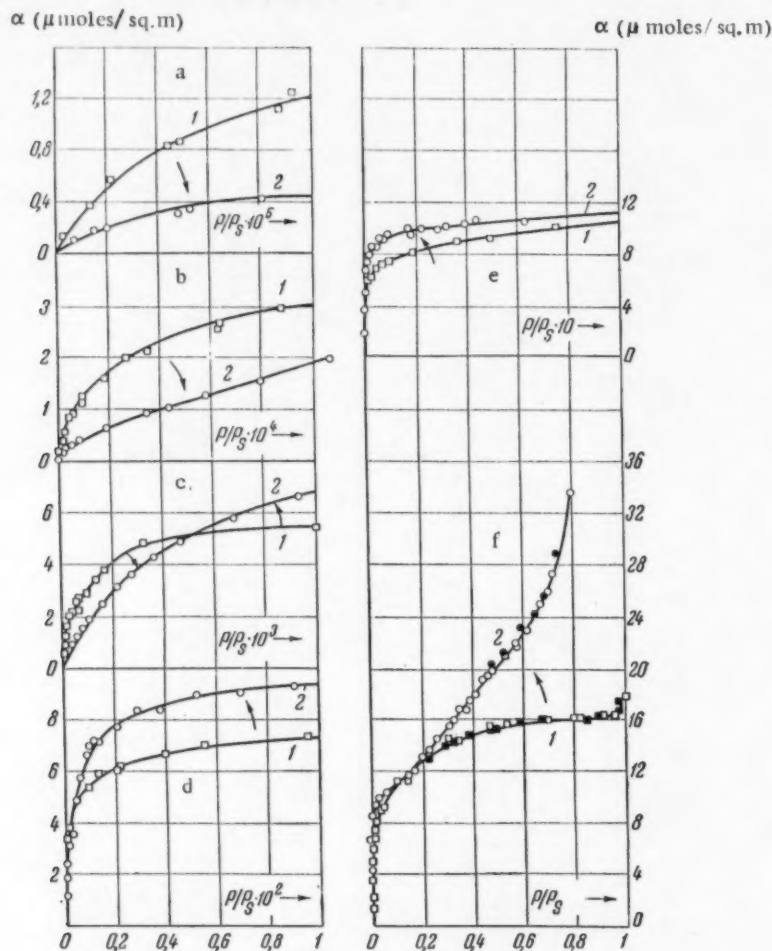


Fig. 6. "Absolute" adsorption isotherms of nitrogen vapor at -195° for samples of 1) finely porous charcoal and 2) Spheron 6 carbon graphitized at 1700° in a stream of hydrogen. The arrows indicate the direction in which the form of the isotherm changes in passage from charcoal to carbon black.

of the surface of the original carbon. The presence of various surface compounds on the original carbon sample, by increasing the distances between adsorbate molecules and carbon atoms of graphite crystallites, lowers the adsorption energy [3]. Hence, for a given value of θ , the adsorption isotherm for the original sample in this region (from $\theta \approx 0.55$ to 1), and also in the region of $\theta > 1$, is displaced to the right, i.e., in the direction of higher p/p_s .

The differences between the adsorption isotherms of nitrogen vapor on original and graphitized Ukhtinsk channel carbon [2] are analogous to those described above.

The parts played by these factors are indicated by the results of the investigation [43] on the adsorption of argon vapor on graphitized carbon that has been oxidized in a stream of oxygen. In Fig. 7 the absolute adsorption

isotherm that we have calculated from these data is compared with adsorption isotherms for ungraphitized and graphitized carbons. It occupies an intermediate position, and the wave in the multimolecular region is less notable for the oxidized sample than for the unoxidized graphitized carbon.

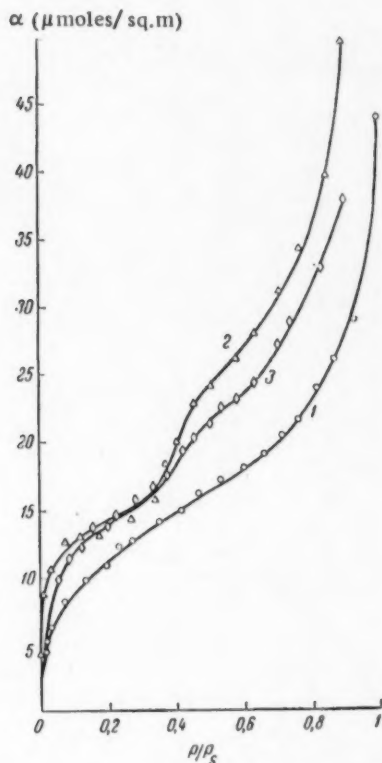


Fig. 7. Absolute adsorption isotherms of argon vapor on samples of Sterling FT carbon: 1) original; 2) graphitized at 2700°; 3) graphitized at 2700° and then oxidized. Constructed from data in [43].

Methane Vapors on Homogeneous Surfaces of Graphitic Bodies at Various Temperatures. It will be seen from the above that by the graphitization of carbons we may obtain a homogeneous surface and determine absolute adsorption isotherms. It is of interest to investigate for such homogeneous surfaces the adsorption isotherms of various simple gases at various temperatures, particularly at temperatures above and below the critical temperature of the adsorption layer.

It was found that the only sample which had been studied in this respect over the whole p/p_s range was P-33 carbon roasted at 2700°. From the data of [24, 29] we calculated absolute isotherms for the adsorption of nitrogen, argon, and krypton vapors on this carbon, these being expressed as a function of p/p_s for low values of θ at -195° and -183° in Fig. 9. The adsorption isotherms of nitrogen vapor obey Henry's law for p/p_s values up to $5 \cdot 10^{-5}$ and for θ values up to 0.1. The form of the isotherms then changes: the adsorption rises sharply and an upward bend appears on the isotherms. The bending of adsorption isotherms, already noted in [44], was explained by Hill [45] and de Boer [46], who obtained an equation for the adsorption isotherm which describes this range of coverage very well. The constants of this equation permit the determination of the ratio of the constants of the van der Waals

We shall now compare the adsorption properties of graphitized carbons treated at various temperatures. In Fig. 8 we compare the absolute adsorption isotherms of nitrogen vapor at -195° on Spheron 6 and P-33 carbons, both graphitized at 1700°, with isotherms on Graphon carbon* [28] and P-33 carbon graphitized at 2700° [5, 24], recalculated per unit surface area. At low values of θ (Figures 8a and 8b) the absolute isotherms on P-33 carbons graphitized at 2700° are not coincident.

Thus, up to $p/p_s = 2 \cdot 10^{-6}$, i.e., up to $\theta = 0.02$, the absolute isotherm for P-33 (1700°) is not linear and is higher than the isotherm for P-33 (2700°). Also, it does not show the bend at $p/p_s = 6 \cdot 10^{-5}$, which is characteristic for P-33 (2700°). In the p/p_s range from $1 \cdot 10^{-4}$ to 0.45, i.e., in the θ range from 0.3 to 1.5, the absolute isotherms for the P-33 carbons coincide.

The absolute adsorption isotherm of nitrogen vapor on Spheron 6 (1700°) coincides with the P-33 isotherms at $p/p_s > 5 \cdot 10^{-3}$, i.e., at $\theta > 0.7$. For low values of θ there are no data for Graphon carbon [28], but over the whole of the θ range studied (0.8-3.5) the absolute adsorption isotherms of nitrogen vapor on Graphon and Spheron 6 (1700°) carbons coincide, which is to be explained by the closeness in size of the crystallites [5, 6]. The difference between the absolute isotherms on the P-33 carbons roasted at different temperatures is probably associated with the fact that the crystallites of P-33 carbon (2700°) are about 50% larger than the crystallites of P-33 (1700°) [5, 6]; P-33 carbon (2700°) is still more homogeneous. The coincidence of the absolute isotherms for different graphitized carbons is observed only when the rough parts of the surface have been covered.

Adsorption of Nitrogen, Argon, Krypton, and

Methane Vapors on Homogeneous Surfaces of Graphitic Bodies at Various Temperatures. It will be seen from the above that by the graphitization of carbons we may obtain a homogeneous surface and determine absolute adsorption isotherms. It is of interest to investigate for such homogeneous surfaces the adsorption isotherms of various simple gases at various temperatures, particularly at temperatures above and below the critical temperature of the adsorption layer.

It was found that the only sample which had been studied in this respect over the whole p/p_s range was P-33 carbon roasted at 2700°. From the data of [24, 29] we calculated absolute isotherms for the adsorption of nitrogen, argon, and krypton vapors on this carbon, these being expressed as a function of p/p_s for low values of θ at -195° and -183° in Fig. 9. The adsorption isotherms of nitrogen vapor obey Henry's law for p/p_s values up to $5 \cdot 10^{-5}$ and for θ values up to 0.1. The form of the isotherms then changes: the adsorption rises sharply and an upward bend appears on the isotherms. The bending of adsorption isotherms, already noted in [44], was explained by Hill [45] and de Boer [46], who obtained an equation for the adsorption isotherm which describes this range of coverage very well. The constants of this equation permit the determination of the ratio of the constants of the van der Waals

* Graphon carbon was obtained by roasting channel carbon at 3000°.

two-dimensional equation of state a_2/b_2 and the calculation of the critical temperature of the layer [24, 29]. An equation of this type was obeyed in [24, 29] for θ ranging from 0.1 to 0.5, and for $\theta > 0.5$ the Langmuir equation was valid.* The adsorption isotherms of argon vapor are close to those of nitrogen for p/p_s values up to $5 \cdot 10^{-5}$ and θ values up to 0.1.

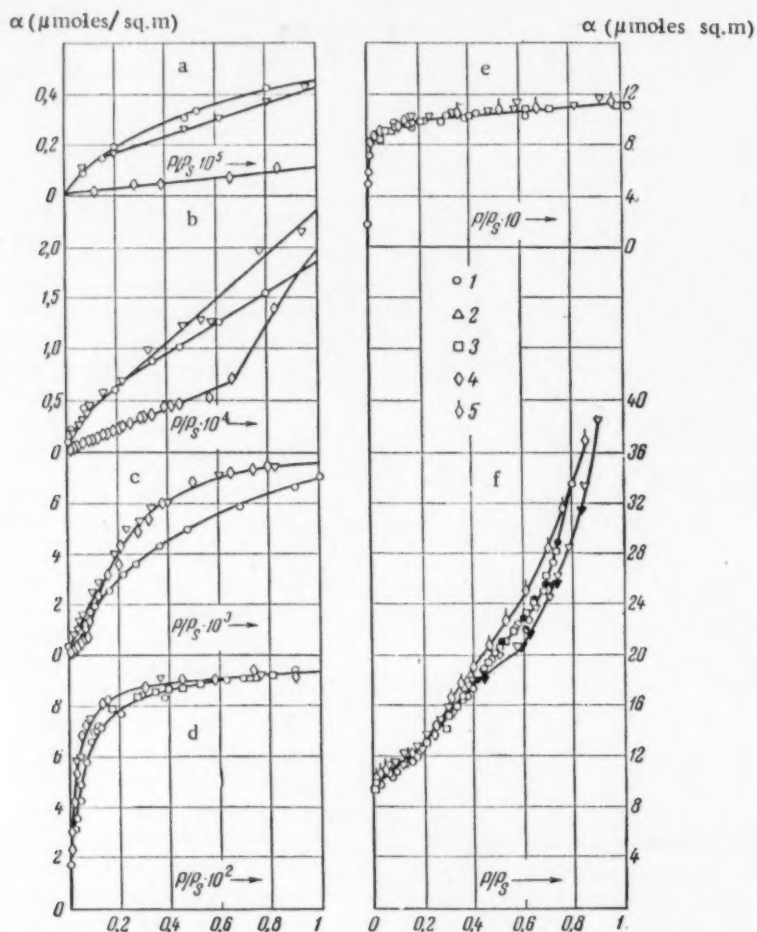


Fig. 8. Absolute adsorption isotherms of nitrogen vapor at -195° for 1) Spheron 6 and 2) P-33 carbons graphitized at 1700° and for 3) Graphon [28], 4) P-33 [24], and 5) P-33 [5] carbons graphitized at 2700° .

The adsorption isotherms of krypton vapor are of special interest because they were measured in [29] at above and below the critical temperature.** For p/p_s values up to $5 \cdot 10^{-4}$ and θ values up to 0.1 these isotherms are linear and differ little from one another. After this the -195° isotherm (below the critical temperature) rises sharply at constant pressure, whereas the -183° isotherm (above the critical temperature) rises as a smooth curve. The authors explain the abrupt rise in adsorption of krypton vapor at -195° at constant vapor pressure by a two-dimensional phase transition.***

*Over the whole of this range the isotherms are described by equations given in [38].

**The critical temperature of the adsorption layer of krypton on graphitized carbon is -188° according to [26] and -191° according to [29], i.e., is close to -190° .

***The applicability of the Langmuir equation to the adsorption isotherms of nitrogen, argon, and krypton vapors at high θ is explained by Ross and Winkler on the view that interaction between adsorbate molecules in this region does not change with rise in θ because surface sites that are surrounded in like manner by adsorbed molecules are being filled.

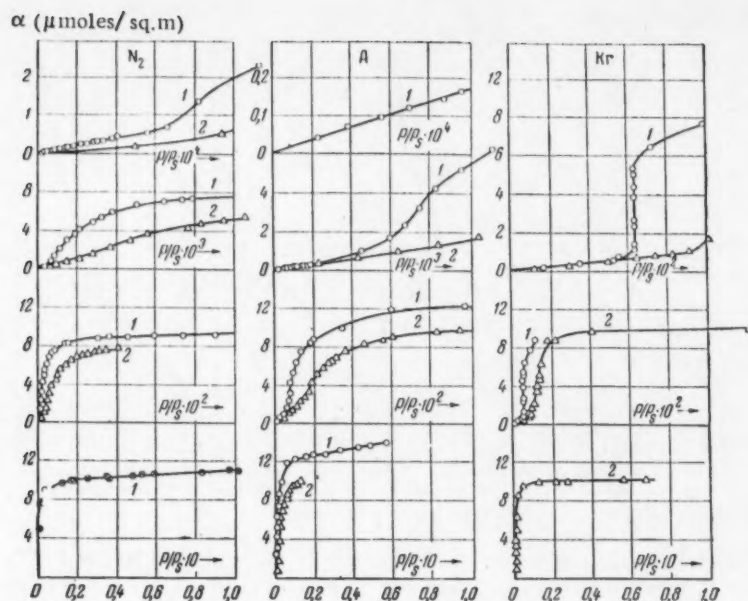


Fig. 9. Absolute isotherms for the adsorption of nitrogen, argon, and krypton vapors on P-33 carbon graphitized at 2700°: 1) at -195° and 2) at -183° and at low values of θ (according to the data of [5, 24, 29]).

Fig. 10 gives the absolute adsorption isotherms of nitrogen, argon, and krypton vapors at -183° as a function of the pressure p . The closeness of the adsorption isotherms of nitrogen and argon vapors is to be explained by the fact that these vapors have very similar adsorption energies and critical temperatures [24, 25]. The adsorption of krypton, which has a much higher adsorption energy and critical temperature, is much greater than that of nitrogen and argon vapors at the same pressure.

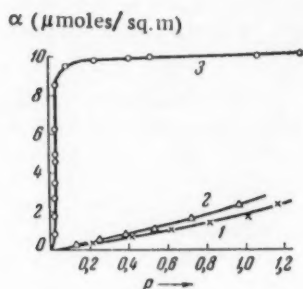


Fig. 10. Absolute adsorption isotherms of 1) argon, 2) nitrogen, and 3) krypton vapors on P-33 carbon graphitized at 2700° (adsorption at -183°) constructed from the data of [24, 29].

of krypton, so that at -195° the steps can be clearly seen. At -166° , close to the boiling point of liquid methane, the isotherm is only wavelike. Hence, the form of the adsorption isotherms of vapor depends both on the degree of homogeneity of the surface of the graphitic body and on the adsorption energy and critical temperature of the adsorbate in the adsorption layer.

An investigation of the equations of the adsorption isotherms of nitrogen, argon, and krypton vapors on graphitized carbon black which take account of adsorbate-adsorbate interaction [38] will be described in a future paper.

Fig. 11 gives the adsorption isotherms of nitrogen and argon vapors at -195° [5] and krypton vapor at -183° [26] on P-33 carbon (2700°) over the whole p/p_s range, as recalculated by us for unit surface. The higher the critical temperature of the adsorbed monolayer, the more clearly is the stepwise character of the adsorption isotherms on a given carbon expressed. Thus, whereas the adsorption isotherms of nitrogen and argon vapors are only wavelike, the adsorption isotherm of krypton vapor, even when measured at a higher temperature, has already two well-defined steps at $p/p_s = 0.5$ and 0.9 characterizing the filling of the second and third layers. In Fig. 11 on the right we give adsorption isotherms of methane vapor on artificial graphite (calculated per gram) at -195° and -166° [47]. The critical temperature of an adsorbed monolayer of methane is higher than that

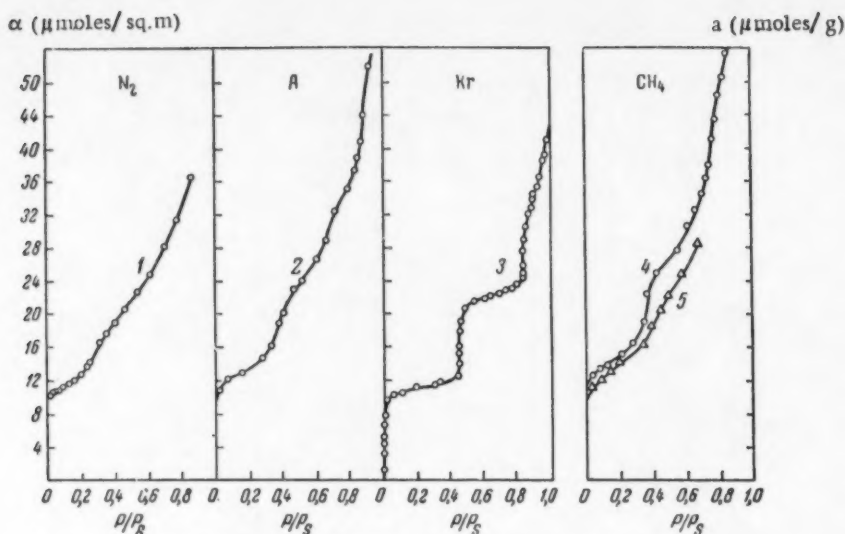


Fig. 11. Absolute adsorption isotherms on P-33 carbon graphitized at 2700° for 1) nitrogen and 2) argon vapors at -195° according to [5] and 3) krypton vapor at -183° according to [26]. The right-hand graph represents adsorption isotherms of methane vapor calculated per gram (the scale for a is twice as great as for α) for artificial graphite at 4) -195° and 5) -166° (data from [47]).

The authors express their thanks to N. N. Avgul* for a discussion of the results.

SUMMARY

1. Roasting carbon blacks at 1700° in a stream of hydrogen considerably reduces surface roughness and makes the surface more homogeneous. Roasting charcoal under these conditions destroys part of its pores and considerably reduces the pore volume. On charcoal the adsorption isotherm of nitrogen vapor rises more steeply than on carbon black.

2. Isotherms for the adsorption of krypton and methane vapors on graphitized bodies of homogeneous surface below the critical temperature of the adsorption layer have a stepwise form. Above the critical temperature there are no breaks in the isotherms, but they retain the wavelike character.

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CAPILLARY CONDENSATION OF VAPORS IN HIGHLY DISPERSED SYSTEMS

COMMUNICATION 3. CAPILLARY CONDENSATION IN CELLS FORMED BY TWO SPHERES OF DIFFERENT RADII IN CONTACT

L. V. Radushkevich

We have previously calculated [1] the volumes of liquid formed in the capillary condensation of vapor near the point of contact of two spherical particles of equal radii. The calculation was based on the condition of thermodynamic equilibrium in this system, so that it was possible to apply Kelvin's equation. We considered also the possibility of making use of some approximate calculations [2], but we showed that they could yield values for the volumes which were considerably in error. In the present paper we give the calculation of volumes of liquid for the case in which the spheres in contact have different radii. This calculation is necessary in order to make the closest possible approximation to conditions in actual dispersed systems formed by spherical particles of different sizes in contact, for which the radius distribution law is known. This more general problem is solved by the same methods as those used in the first communication [1]; in the analysis of the results, attention was paid to the possibility of deriving, from the general equations, the results found previously for the special case of two particles of equal radii.

1. Capillary-condensate Volumes for a Cell Formed by Two Spheres of Different Radii in the Limiting Case

We shall first examine the calculation of volumes of capillary condensate for cells formed by two spheres of different radii R_1 and R_2 for the case when $p/p_s = 1$. In what follows we shall denote the ratio of radii R_2/R_1 by λ , and we shall always assume that $R_2 > R_1$, so that $\lambda > 1$.

Under the condition of complete saturation, $C \rightarrow \infty$ and $K = 0$, the surface of zero curvature is again a catenoid [1] and the meniscus profile is a catenary, which is disposed unsymmetrically with respect to the tangent at the point of contact (Fig. 1). As the problem nevertheless remains an axially symmetrical one with the axis joining the centers of the spheres, we shall again transfer all constructions to a plane, and the first stage of the calculation is the finding of segments demarcating volumes. For all values of λ let us use the equation to the catenary in the form

$$y = a \cdot \cosh x/a.$$

In such a case, with change in λ the relative positions of a cell formed by two spheres and the y axis will change. Whereas in the previous case, in which $\lambda = 1$, the y axis passes through the point of contact of the spheres, in the present case with increase in λ the y axis is displaced to the left in the direction of the smaller sphere, and the abscissa of the point of contact increases continuously (see Fig. 1).

It will be shown further that the position for which $x_0 = R_1$ corresponds to $\lambda = 5.78$; for different values of λ we can accordingly distinguish four cases:

$$\begin{aligned} \lambda &= 1; & x_0 &= 0, \\ 1 < \lambda < 5.78; & x_0 &= R_1 - x_M - \sqrt{R_1^2 - y_M^2}; \end{aligned}$$

$$\lambda = 5,78; \quad x_0 = R_1;$$

$$\lambda > 5,78; \quad x_0 = R_1 + x_M + \sqrt{R_1^2 - y_M^2}.$$

Here x_M, y_M are the coordinates of the point of contact of the catenary and the left circle, and x_N, y_N are the corresponding coordinates for the right circle. We shall require also the abscissas of the centers of the circles x_A and x_B , and also the heights of the segments h_1 and h_2 . Taking the above considerations concerning the position of the y axis into account, we may lay down the following conditions for the absolute values of the segments in the general case, for which $\lambda \geq 1$:

$$\begin{aligned} x_0 &= R_1 \mp x_M \mp \sqrt{R_1^2 - y_M^2}; \\ x_B \pm x_A &= R_1 + R_2; \quad h_1 = x_0 \pm x_M; \\ h_2 &= x_N - x_0. \end{aligned}$$

The upper signs correspond to $\lambda < 5,78$, and the lower signs to $\lambda > 5,78$. For $\lambda = 5,78$ we have $x_0 = R_1$; $x_A = 0$; $x_M = 0$.

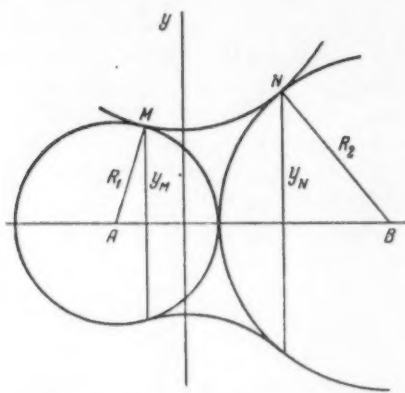


Fig. 1.

We may show also that

$$\cosh z_2 = \sqrt{\lambda} \cdot \cosh z_1. \quad (2)$$

By expressing the hyperbolic cosine in the exponential form and remembering that z_2 is always greater than zero, from (2) we obtain:

$$z_2 = \ln [\sqrt{\lambda} \cosh z_1 + \sqrt{\lambda \cosh^2 z_1 - 1}].$$

This equation enables us to eliminate z_2 from Equation (1'), and we then obtain an equation for one unknown quantity z_1 at given λ .

$$\begin{aligned} (\sqrt{\lambda} \sqrt{\lambda \cosh^2 z_1 - 1} \pm \sqrt{\cosh^2 z_1 - 1}) \cosh z_1 &= (1 + \lambda) \cosh^2 z_1 - \\ &- \ln (\sqrt{\lambda} \cosh z_1 + \sqrt{\lambda \cosh^2 z_1 - 1}) - z_1. \end{aligned} \quad (3)$$

When $z_1 < 0$ the upper signs must be taken, and when $z_1 > 0$ the lower signs must be taken. It can be shown that for $\lambda = 1$ Equation (3) passes into the relationship (for $z_1 < 0$):

$$\frac{1}{2} \sinh 2z_1 = \cosh^2 z_1 - z_1,$$

which is equivalent to Equation (8) of the first communication for a system of two equal spheres.

It is better to write Equation (3) in the form:

$$z_1 = \pm [(1 + \lambda) \cosh^2 z_1 - (\sqrt{\lambda} \sqrt{\lambda \cosh^2 z_1 - 1} \pm \sqrt{\cosh^2 z_1 - 1}) \cosh z_1 - \ln (\sqrt{\lambda} \cosh z_1 + \sqrt{\lambda \cosh^2 z_1 - 1})]. \quad (4)$$

The problem amounts to finding the values of a, x_M , and x_N , from which it is easy to find the other segments demarcating the volumes. For convenience, we shall first determine the values of the ratios $z_1 = x_M/a$ and $z_2 = x_N/a$. The conditions for contact between the two circles and the catenary lead to the relationship:

$$\sinh z_2 \cosh z_2 - \sinh z_1 \cosh z_1 = R_1/a + R_2/a - z_2 + z_1. \quad (1)$$

By the use of known properties of hyperbolic functions and by the application of the conditions for contact, we find:

$$\begin{aligned} (\sqrt{\lambda} \sqrt{\lambda \cosh^2 z_1 - 1} \pm \sqrt{\cosh^2 z_1 - 1}) \cosh z_1 &= \\ &= (1 + \lambda) \cosh^2 z_1 - z_2 + z_1. \end{aligned} \quad (1')$$

Here, for $z_1 < 0$ the upper signs must be taken. This equation is easily solved graphically. On the left we have an equation to a straight line, and on the right the equation to a curve associated with the parameter λ and the variable $\cosh z_1$. It can be shown that there is only one point of intersection of the two lines in the real region, i.e., at given λ there is only one real root of Equation (4). In the special case in which $x_M = 0$ or $z_1 = 0$, Equation (4) becomes

$$1 + \lambda - \sqrt{\lambda} \sqrt{\lambda - 1} - \ln(\sqrt{\lambda} + \sqrt{\lambda - 1}) = 0.$$

The graphical solution of this equation gives $\lambda = 5.78$, which corresponds to the special case already considered in which the y axis passes through the center of the smaller sphere. For given λ , having found the value of z_1 from (4), we substitute this value in (2) and find z_2 . Table 1 gives pairs of values of z_1 and z_2 for various values of λ .

TABLE 1

λ	z_1	z_2
1,00	-0,640	+0,640
1,25	-0,545	+0,742
1,50	-0,468	+0,826
2,00	-0,354	+0,966
4,00	-0,113	+1,324
5,00	-0,043	+1,445
5,78	-0,000	+1,524
7,00	+0,062	+1,635
8,00	+0,102	+1,705
10,00	+0,145	+1,830

TABLE 2

λ	U_{12}	$\gamma = U_{12}/U_{\lambda=1}$
1,00	0,4176	1,00
1,25	0,57523	1,38
1,50	0,74693	1,79
2,00	1,09148	2,62
4,00	2,42572	5,82
5,00	3,06523	7,34
5,78	3,5555	8,52
7,00	4,325	10,35
8,00	5,000	12,0
10,00	6,7301	16,1

For the calculation of capillary-condensate volumes we introduce the dimensionless quantities:

$$X_M = x_M/R_1; \quad Y_M = y_M/R_1; \quad H_1 = h_1/R_1; \quad k = a/R_1; \\ X_N = x_N/R_1; \quad Y_N = y_N/R_1; \quad H_2 = h_2/R_1; \quad X_0 = x_0/R_1.$$

The volume of liquid held near the point of contact is expressed in terms of the volume of the catenoid V_K and the two volumes W_1 and W_2 of the spherical segments in the following way: $V = V_K - (W_1 + W_2)$.

From simple geometric relationships for bodies of rotation it follows that

$$V_K = \frac{1}{4} \pi a^3 (\sinh 2z_1 + \sinh 2z_2 + 2z_1 + 2z_2); \\ W_1 = \frac{1}{6} \pi (3y_M^2 + h_1^2)h_1; \quad W_2 = \frac{1}{6} \pi (3y_N^2 + h_2^2)h_2.$$

The required volume of liquid V is therefore expressed as

$$V = \frac{1}{3} \pi R_1^3 \left[\frac{3}{4} k^3 (\sinh 2z_1 + \sinh 2z_2 + 2z_1 + 2z_2) - \frac{1}{2} (H_1(3Y_M^2 + H_1^2) + H_2(3Y_N^2 + H_2^2)) \right]. \quad (5)$$

The individual quantities entering into this equation are found as follows:

- 1) z_1 and z_2 from Equations (4) and (2) as indicated above;
- 2) k from the equation $k = (\cosh^2 z_1)^{-1/2}$, which follows from Equation (1) after application of the conditions of contact and elimination of hyperbolic sines;
- 3) Y_M from the equation to the catenary $Y_M = k \cosh z_1$;
- 4) Y_N from the equation $Y_N = \sqrt{\lambda} Y_M$;
- 5) H_1 and H_2 from the conditions given previously for h_1 and h_2 after substitution of the values found for X_1 , X_2 , Y_1 , and Y_2 and consideration of the signs for different λ regions.

Equation (5) can be written as

$$V = \frac{1}{3} \pi R_1^3 U_{12}, \quad (6)$$

in which U_{12} is a dimensionless function having the form:

$$U_{12} = \frac{3}{4} k^3 (\sinh 2z_1 + \sinh 2z_2 + 2z_1 + 2z_2) - \frac{1}{2} [H_1 (3Y_M^2 + H_1^2) + H_2 (3Y_N^2 + H_2^2)]. \quad (7)$$

We calculated U_{12} for different values of λ , and the results are given in Table 2. The last column gives values of γ , the ratio of U_{12} to the corresponding value at $\lambda = 1$. As can be seen from these final results, the capillary-condensate volume at $p/p_s = 1$ for a cell formed by two spheres of different radii is appreciably greater than for a cell formed by equal spheres. With increase in λ this volume increases substantially. Thus, a difference in radii of 25% gives an increase in the volume of 38%, as will be seen from Table 2. For values of λ ranging from 1.00 to 8.00, the function U_{12} has an almost linear course.

2. General Case of Capillary Condensation for Cells Formed by Two Spheres of Different Radii

In the general case, $p/p_s < 1$ and C finite, the layer of liquid formed between two spheres of different radii in contact during capillary condensation has the form of a nodoid with a meniscus of trochoid profile, as also for spheres of equal radii (see first communication). The problem now amounts to the determination of one of the radii of the trochoid as a function of relative pressure, after which it will be possible to calculate volumes of liquid at different p/p_s . As the case of contact between spheres of different radii is a generalization of the case of equal radii, the course of the solution of this problem is in principle the same as that described in the first communication.

As before, let us write $\beta = C/R_1$, and it is clear that again we have $C = r_2 - r_1$, in which r_1 and r_2 are the small and large radii of the trochoid. As before, we shall introduce the ratio of the radii of the spheres, $\lambda = R_2/R_1$ ($\lambda \geq 1$). In Fig. 2 by geometric construction it is easy to find relationships giving the conditions for contact between the arc of the trochoid and the two circles in contact. Together with the conditions of constancy of distance between the centers of the circles, these relations form a system of equations having five unknowns:

$$\left. \begin{aligned} z_A - \sqrt{R_2^2 - r_M^2} &= r_1 \Phi(\alpha, \varphi_M) - r_2 \psi(\alpha, \varphi_M); \\ r_M (R_2^2 - r_M^2)^{-1/2} &= (r_1 r_2 - r_M^2) [(r_M^2 - r_1^2) (r_2^2 - r_M^2)]^{-1/2}; \\ z_B - \sqrt{R_1^2 - r_N^2} &= r_1 \Phi(\alpha, \varphi_N) - r_2 \psi(\alpha, \varphi_N); \\ r_N (R_1^2 - r_N^2)^{-1/2} &= (r_1 r_2 - r_N^2) [(r_N^2 - r_1^2) (r_2^2 - r_N^2)]^{-1/2}; \\ z_A + z_B &= R_1 + R_2. \end{aligned} \right\} \quad (8)$$

Here $\Phi(\alpha, \varphi)$ and $\psi(\alpha, \varphi)$ are values of definite elliptical integrals for the points of contact M and N [1]. It is quite obvious that Equation (8) is a generalization of the previous conditions (23) and (24) of the first communication, in which special case of $R_1 = R_2$ is examined.

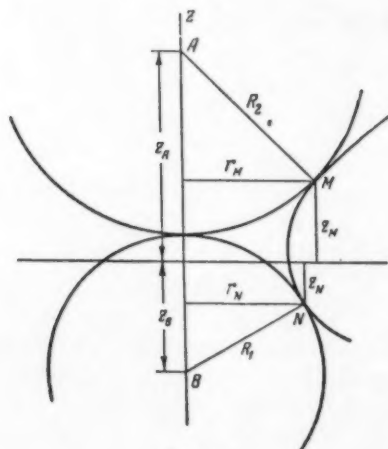


Fig. 2.

As an unknown we introduce the dimensionless ratio $x = r_1/R_1$. Combining the first and third of Equations (8) and taking the fifth into consideration, we may eliminate four unknowns and, after simple rearrangements, obtain a single equation for x at a given value of β :

$$\begin{aligned} 1 + \lambda - \sqrt{\lambda^2 - \frac{x(x+\beta)}{1+\beta/\lambda}} - \\ - \sqrt{1 - \frac{x(x+\beta)}{1+\beta}} = x [\Phi(\alpha, \varphi_M) - \\ - \psi(\alpha, \varphi_M) + \Phi(\alpha, \varphi_N) - \psi(\alpha, \varphi_N)] - \\ - \beta [\psi(\alpha, \varphi_M) + \psi(\alpha, \varphi_N)]. \end{aligned} \quad (9)$$

The angles α , φ_M and φ_N can be readily related to \underline{x} and β by the use of the known expression for the modulus and argument of elliptical integrals. After simple rearrangements we obtain:

$$\left. \begin{aligned} \sin \alpha &= \sqrt{1 - \left(\frac{x}{x+\beta}\right)^2}; \\ \sin \varphi_M &= \frac{1}{\sin \alpha} \sqrt{1 - \frac{\cos \alpha}{1+\beta/\lambda}}; \\ \sin \varphi_N &= \frac{1}{\sin \alpha} \sqrt{1 - \frac{\cos \alpha}{1+\beta}}. \end{aligned} \right\} \quad (10)$$

We may show that Equation (9) is converted into the expression given in the first communication for $R_1 = R_2$, if we substitute $\lambda = 1$ in Equation (9). After division by 2, Equation (9) becomes

$$1 - \sqrt{1 - \frac{x(x+\beta)}{1+\beta}} = x [\Phi(\alpha, \varphi_0) - \psi(\alpha, \varphi_0)] - \beta \psi(\alpha, \varphi_0),$$

i.e., is identical with Equation (27) of the first communication. At the same time the expressions for φ_M and φ_N pass into

$$\sin \varphi_M = \sin \varphi_N = \sin \varphi_0 = \frac{1}{\sin \alpha} \sqrt{1 - \frac{\cos \alpha}{1+\beta}}.$$

Equation (9) can be transformed into a more convenient form by the introduction of

$$\beta/\lambda = \beta' \text{ and } x/\lambda = x'.$$

If we then transfer terms containing the variables \underline{x} and β to one side of Equation (9) and the variables x' and β' to the other, we obtain identical functional expressions. We therefore name a function as follows:

$$F(y, \beta) = 1 - \sqrt{1 - \frac{y(y+\beta)}{1+\beta}} - y [\Phi(\alpha, \varphi) - \psi(\alpha, \varphi)] + \beta \psi(\alpha, \varphi)$$

with the conditions that

$$\sin \alpha = \sqrt{1 - \left(\frac{y}{y+\beta}\right)^2} \text{ and } \sin \varphi = \frac{1}{\sin \alpha} \sqrt{1 - \frac{\cos \alpha}{1+\beta}}.$$

Equation (9) then takes the form:

$$F(y_1, \beta) = -\lambda \cdot F(y_2, \beta') \quad (11)$$

with the conditions that $\alpha = \alpha'$; $\sin \alpha = \sin \alpha'$,

$$\sin \varphi_N = \frac{1}{\sin \alpha} \sqrt{1 - \frac{\cos \alpha}{1+\beta}}; \quad \sin \varphi_M = \frac{1}{\sin \alpha'} \sqrt{1 - \frac{\cos \alpha'}{1+\beta'}}. \quad (12)$$

Equation (12) is convenient for the finding of unknown \underline{x} at given β and λ . The solution is carried out graphically: for given β we graph the function $F(y_1)$, and then for given λ we graph the function $-\lambda F(y_2)$. The intersection of the two curves then gives the value of $y_1 = x$. It should be noted that when $\lambda = 1$ the function $F(y, \beta)$ becomes zero and Equation (11) becomes an identity. Table 3 gives values of \underline{x} obtained in the way indicated for different values of β and for different values of λ . For comparison purposes it gives also the values obtained previously for \underline{x} at $\lambda = 1$ and the parameters \underline{a} of the catenary in the limiting case of $\beta \rightarrow \infty$, which coincide with the small radius of the degenerate trochoid. It must be mentioned that the accuracy of the graphical solution was not high,

so that the third significant figure in the values of \underline{x} is not altogether reliable. However, if more precise values are required, the accuracy can be correspondingly raised. If the accuracy required is not very high, Equation (11) may be solved by the selection of values of y_1 known tentatively from the data cited. Some of the values in Table 3 were obtained from graphs of the family of curves $\underline{x} = f(\beta)$.

TABLE 3

β	$\lambda=1.00$	$\lambda=1.25$	$\lambda=1.50$	$\lambda=2.00$	$\lambda=4.00$
	\underline{x}	\underline{x}	\underline{x}	\underline{x}	\underline{x}
0,003	0,051	0,0515	0,05286	0,0552	0,061
0,005	0,067	0,067	0,071	0,076	0,081
0,010	0,093	0,098	0,1025	0,1084	0,1163
0,020	0,128	0,136	0,1405	0,147	0,163
0,050	0,194	0,2045	0,2125	0,220	0,2495
0,100	0,250	0,2695	0,2807	0,3013	0,339
0,200	0,325	0,3586	0,3712	0,3948	0,440
0,300	0,370	0,406	0,420	0,447	0,508
0,400	0,404	0,440	0,458	0,490	0,564
0,500	0,432	0,465	0,489	0,5235	0,6115
0,600	0,455	0,489	0,5172	0,5538	0,6432
0,800	0,485	0,525	0,556	0,595	0,690
1,000	0,502	0,552	0,585	0,632	0,730
1,500	0,530	0,6165	0,654	0,720	0,830
∞	0,681	0,7531	0,8095	0,8845	0,9874

The value found for $x = r_1/R_1$ enables us to determine the value of $r_2/R_1 = \beta + x$, and then all the quantities necessary for the calculation of the volumes of liquid near the points of contact of the spheres.

The volume of liquid V is expressed, as before, by the sum

$$V = V_H - (W_1 + W_2),$$

in which V_H is the volume of the nodoid between the points M and N ; W_1 and W_2 are the two different volumes of spherical segments. The volume V_H can be conveniently expressed as the sum of volumes lying between $r = r_1$ and $r = r_M$ and $r = r_1$ and $r = r_N$, i.e.,

$$V_H = \pi \int_0^M r^2 dz + \pi \int_0^N r^2 dz =$$

$$= \pi \int_{r_1}^{r_N} \frac{r_1 r_2 r^2 - r^4}{(r_2^2 - r^2)(r^2 - r_1^2)} dr + \pi \int_{r_1}^{r_M} \frac{r_1 r_2 r^2 - r^4}{(r_2^2 - r^2)(r^2 - r_1^2)} dr.$$

For finding the two integrals we may use the transformed Equation (30) of the first communication, i.e., Equation (33); it is then found that

$$V_H = 1/3 \pi R_1^3 \{x^2 (\beta + x) [\Phi(\alpha', \varphi_{01}) + \Phi(\alpha'', \varphi_{02})] + 1/2 \beta (\beta + 2x) x_{01} \sin 2\varphi_{01} +$$

$$+ x_{02} \sin 2\varphi_{02} - [2\beta^2 + x(\beta + x)] (\beta + x) [\psi(\alpha', \varphi_{01}) + \psi(\alpha'', \varphi_{02})]\},$$

in which α' and φ_{01} refer to the point N and α'' and φ_{02} to the point M ; also, it is here postulated that $x_{01} = r_N/R_1$ and $x_{02} = r_M/R_1$. We find the volumes of the spherical segments by first calculating their heights:

$$h_1 = R_1 (1 - \sqrt{1 - x_{01}^2}) \text{ and } h_2 = R_1 (\lambda - \sqrt{\lambda^2 - x_{02}^2}),$$

we then have

$$W_1 = 1/3 \pi R_1^3 [2 - \sqrt{1 - x_{01}^2} (2 + x_{01}^2)];$$

$$W_2 = 1/3 \pi R_1^3 [2\lambda^3 - \sqrt{\lambda^2 - x_{02}^2} (2\lambda^2 + x_{02}^2)].$$

The volume of liquid between the spheres is finally expressed as

$$V = 1/3 \pi R_1^3 U_{12}, \quad (13)$$

in which

$$U_{12} = (2 + x_{01}^2) \sqrt{1 - x_{01}^2} + (2\lambda^2 + x_{02}^2) \sqrt{\lambda^2 - x_{02}^2} + x^2 (x + \beta) [\Phi(\alpha', \varphi_{01}) + \Phi(\alpha'', \varphi_{02})] + 1/2 \beta (\beta + 2x) (x_{01} \sin 2\varphi_{01} + x_{02} \sin 2\varphi_{02}) - [(2\beta^2 + x(x + \beta)) (x + \beta) [\psi(\alpha', \varphi_{01}) + \psi(\alpha'', \varphi_{02})] - 2(1 + \lambda^3)]. \quad (14)$$

If we substitute $\lambda = 1$, it will be readily seen that $U_{12} = 2U$, in which U is the function (36) of the first communication, so that as before we shall have $V = 2/3 \pi R_1^3 U$.

In Equation (14) the values of x_{01} and x_{02} are found from

$$x_{01} = \sqrt{\frac{x(\beta + x)}{1 + \beta}} \text{ and } x_{02} = x_{01} \sqrt{\frac{\lambda(1 + \beta)}{\lambda + \beta}}.$$

The value of x is determined as stated above, and α' , φ_{01} , α'' , and φ_{02} are calculated from Equation (10) of this communication, and we have

$$\alpha' = \alpha'' = \alpha \text{ and } \varphi_{01} = \varphi_N; \varphi_{02} = \varphi_M.$$

Table 4 gives values of relative volumes for various values of λ and β , including the case of $\lambda = 1$.

TABLE 4

β	1.00	$\lambda=1.25$	$\lambda=1.50$	$\lambda=2.00$	$\lambda=4.00$
	$U_{12} \cdot 10^3$	$U_{12} \cdot 10^3$	$U_{12} \cdot 10^3$	$U_{12} \cdot 10^3$	$U_{12} \cdot 10^3$
0.005	0.038	0.039	0.040	0.0406	0.0683
0.010	0.120	0.135	0.154	0.1628	0.2373
0.020	0.3446	0.471	0.525	0.605	0.726
0.050	1.864	2.920	3.02	3.121	3.937
0.100	6.878	8.104	8.822	10.282	13.000
0.200	19.806	24.461	25.992	30.569	42.708
0.400	49.344	59.290	68.309	82.214	111.16
0.500	64.974	77.917	89.786	109.541	156.312
0.600	73.898	95.849	110.983	136.602	188.840
0.800	107.676	129.478	148.321	188.537	258.41
1.000	141.318	168.933	193.692	238.977	345.633
1.500	150.364	185.3	235.2	325.93	479.11
∞	417.60	575.23	746.93	1091.48	2425.72

The results show that the differences in the sizes of the spherical particles have an appreciable effect on the volume of liquid near the point of contact. For all values of β , except for the very lowest, a difference of radii of 25% results in an increase in the volume of more than 10%. It follows that in systems of packed spherical particles the effect of polydispersity can be neglected in the calculation of capillary condensation when the dimensions of the spheres of the extreme fractions differ by substantially less than 25%, or when these dimensions are so great that the whole calculation corresponds to the region of very low β ($\beta \leq 0.005$).

In concluding our detailed calculations on the capillary condensation of vapor in cells formed from two spheres, we must point out that these calculations were intended for the description of the process in systems of numerous

packed spherical particles of extremely small radius. In connection with this problem it was necessary to determine the reliability of commonly used simplified methods of calculating volumes of capillary condensate. Our appraisal of these showed that in general they are of little use, and it was therefore necessary to have recourse to rigorous calculation. We use Kelvin's formula for equilibrium, expressed in the general case with the aid of the parameter C ; the relationship found between volumes and β is therefore quite universal. When the values of σ and γ depart from the values given in tables, all our results will remain valid. Comparison with experimental data may enable us to reveal anomalies in the process of capillary condensation in highly dispersed systems of spherical particles. It would be possible to extend our calculations to cases in which incomplete wetting occurs and also to take account of imperfect contact of the particles, if they make contact in a plane and not in a single point. For these cases the methods of calculation described here are again applicable, and it is easy to introduce modifications into the results on the basis of the geometry of the system. It must be noted also that it is clear from the above considerations that there should be no hysteresis in capillary condensation in systems of many spherical particles until the coalescence of menisci occurs. In our further work our results will be applied to the calculation of the process in sorbents such as carbon black, in chains of smoke particles, and in other analogous systems.

SUMMARY

Exact calculations are made of the volumes of capillary condensate at various relative pressures in systems of two spheres of different radii in contact, and it is shown that a difference of 25% in the dimensions of the spheres in contact results in an appreciable increase in the volume of liquid, as compared with the case of spheres of equal radii.

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*Original Russian pagination. See C. B. Translation.

ADSORPTION AND CATALYSIS

COMMUNICATION 1. LIQUID-PHASE HYDROGENATION OF MALEIC AND FUMARIC ACIDS

V. V. Patrikeev, A. A. Balandin, and M. L. Khidekel'

Liquid-phase hydrogenation at atmospheric pressure in presence of heterogeneous catalysts is of enormous practical importance. However, in spite of the large number of investigations carried out in this field, there are still no clear views on comparatively simple questions relating to the mechanism of hydrogenation. The surface concentrations of the reactants have scarcely received consideration, and in the case of successive hydrogenations conclusions are drawn, often without an adequate experimental basis, concerning the effect of adsorption on selectivity, or sequence of hydrogenation.

However, a knowledge of the amount of substance adsorbed on the catalyst may help in the solution of many questions concerning, for example, the effect of solvents and reaction products on mechanism and kinetics and, what is particularly important, may help to elucidate the role of adsorption in the selective or successive addition of hydrogen in the hydrogenation of mixtures. Very little experimental work on this question has been reported. Platonov [1] determined the adsorption of various organic acids on platinum black from aqueous and ethereal solutions. The extent of adsorption was determined by titration of the acid solution, which was filtered from the platinum black after it had been shaken for five minutes and allowed to settle for 20 minutes. The author carried out parallel experiments on hydrogenation in a long-necked flask over platinum black, and he found that for *cis*- and *trans*-isomers and for isomers that form the same hydrogenation products there is a qualitative parallelism between adsorption and rate of hydrogenation. The author points out considerable discrepancies in his experiments.

Stoliarov and Todes [2] proposed to determine the amount of substance adsorbed from a solvent by the consumption of hydrogen in the hydrogenation of the adsorbed substance in a fresh portion of solvent. In the adsorption of styrene from benzene and acetic acid on platinum black, nickel prepared from its formate, and Raney nickel, they found that the amount adsorbed was independent of the bulk concentration of styrene, which they considered to indicate that the catalyst surface was saturated with styrene. A parallelism was found between extent of adsorption and reaction rate. The mean departure in the values found for the adsorption of styrene was 15-18%.

EXPERIMENTAL

For the study of adsorption on a catalyst from the liquid phase under conditions as close as possible to the actual conditions of hydrogenation, we designed an apparatus that was suitable for the investigation of adsorption and hydrogenation on a catalyst. An external view of the apparatus is shown in Fig. 1. The apparatus consists of three sections, 1, 2, and 3, each 100 ml in capacity; these are connected at their lowest parts by the tap 4, which permits the side vessels to be connected in turn to the central vessel or the solutions to be removed from the vessels through the outlet 5. A No. 2 or No. 3 porous plate 6 is sealed in the central vessel, and the upper part of this vessel is closed by a ground cap carrying a four-way tap 7, which, like the tap 4, is of the crescent-bore type. The apparatus is maintained at constant temperature by immersion in a thermostat, and it is connected to a circulation pump (designed by one of us [3]) and to burets containing hydrogen (Fig. 2). By change in the positions of the taps 4 and 7, solution may be transferred from one section to another in the order necessary, without stopping the circulation pump.

The reaction or adsorption is carried out in the vessel 2 over the catalyst, which is situated on the porous plate; vigorous agitation is produced by bubbling hydrogen through the porous plate with the aid of the circulation pump 2

(Fig. 2). The gas burets 1 are attached to the delivery side of the pump. Change of solvent in the reaction vessel can be carried out in 5-6 seconds. The rate of reaction is determined from the absorption of hydrogen with the aid of gas burets or an automatic gas meter.

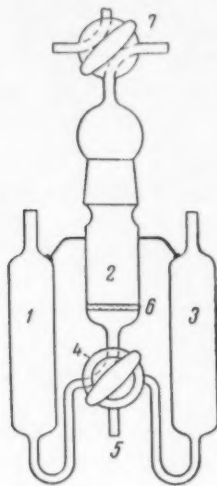


Fig. 1. Apparatus for liquid-phase catalytic-hydrogenation and adsorption.

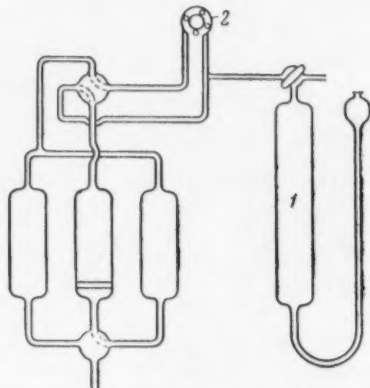


Fig. 2. Diagram of circulatory apparatus.

Using the circulatory apparatus, we hydrogenated eugenol at 19° and atmospheric pressure as a solution in 96% alcohol in presence of 1 g of Raney nickel in order to determine the effect of degree of agitation on reaction rate. It will be seen from Fig. 3 that, for

speeds of rotation of the circulation pump above 280 r.p.m. (diameter of rubber 4 mm), this speed has no effect on the rate of hydrogenation of eugenol. It was shown that there is a direct proportionality between the amount of catalyst and the rate of hydrogenation of eugenol when the amount of catalyst is doubled or tripled.

It may be considered, therefore, that our method is satisfactory for the study of reaction in the kinetic region [4]. The circulatory system has advantages over the more primitive long-necked flask (simplicity of construction, possibility of making various additions without interrupting the reaction, safety) and opens up new possibilities for the study of catalytic processes.

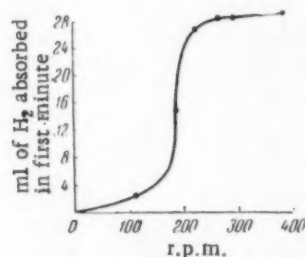


Fig. 3. Relation of rate of hydrogenation of eugenol to degree of agitation; $c_0 = 0.326$ mole/liter; $t = 19^\circ$; $p = 1$ atm.

As a subject for investigation we selected a mixture of fumaric and maleic acids, which give the same product, succinic acid, when hydrogenated. Some work has been reported on the catalytic hydrogenation of the individual acids in solvent [1]. It was found that the cis-acid is hydrogenated more rapidly than the trans-acid. Sokol'skii and Druz' [5], who used the potentiometric method in an investigation of the hydrogenation of an equimolecular mixture of sodium maleate and fumarate over Raney nickel, did not establish successive hydrogenation in the mixture, but suggested that hydrogen added simultaneously to both substances, though one of the compounds hydrogenated more rapidly than the other. In the hydrogenation of a mixture of maleic and fumaric acids over platinum and palladium, Markman [6] used a polarographic method for the analysis of samples taken in the course of reaction, acidified ethanol being employed as supporting medium; he found that maleic acid is hydrogenated preferentially.

We carried out adsorption and hydrogenation at atmospheric pressure and room temperature (19°) in 96% ethanol over 1 g of Raney nickel. Weights of test samples were determined on a torsion balance by a procedure which was developed specially for this purpose and will be described separately. The catalyst was prepared by

leaching a 50 : 50 Ni-Al alloy as completely as possible, grinding the products, and selecting the fraction 0.25-0.5 mm in size. The specific surface of this catalyst was determined previously by the nitrogen-adsorption method; it was 40 sq.m/g.

We used the polarographic method of analysis [7]. As supporting electrolyte we used a buffer mixture of NH_4Cl and NH_4OH of pH 8.2 and unit ionic strength. We used a manual apparatus with a dropping mercury electrode with forced detachment of the drop [8]. Nickel need not be filtered off; it does not interfere in the determination. When the solution for analysis stands for a long time in the air, oxidation occurs with formation of Ni^{2+} ions, which give a wave at 1.1 v; this however, does not interfere with the separation of the waves of the acids being analyzed. In some experiments the solution was titrated with 0.1 N NaOH and account was taken of the volume of hydrogen absorbed. Before the experiment the catalyst was saturated with hydrogen for 20 minutes.

Before starting adsorption experiments, we determined the time required for the establishment of substantially complete adsorption equilibrium. The fumaric acid solution was transferred to the central vessel, thus stirring the catalyst; it was then passed back and analyzed polarographically and by titration. It may be noted that the closeness of the results of these analyses indicates that in the course of the adsorption no appreciable extraction of hydrogen from the catalyst occurred [9]. The time required to pass the solution onto the catalyst and back was five seconds. The operation was then repeated with a new solution until there was constancy of concentrations in the solution analyzed. As will be seen from Fig. 4, a time of 10 seconds was found. Taking this fact into account, we decided to give an "exposure" of the solution above the catalyst of 20 seconds, so that there was some time "in hand".

TABLE 1

Data on the Adsorption and Hydrogenation of the Individual Acids

Experiment	Original amount of maleic acid (g)	Original amount of fumaric acid (g)	Original amount of succinic acid (g)	Amount of acid adsorbed (g)			Amount of hydrogenated acids (g)			Duration of hydrogenation (seconds)
				maleic	fumaric	succinic	maleic	fumaric	succinic	
1	0,3583	—	—	0,1025	—	—	—	—	—	—
2,3	0,5374	—	—	0,1087	—	—	0,2409	—	—	180
4,5	—	0,5392	—	—	0,0835	—	—	0,1843	—	440
6	0,4300	—	0,1276	0,0878	—	0,0135	—	—	—	—
7	—	0,4599	0,0851	—	0,0681	0,0169	—	—	—	—

We investigated the possibility of the isomerization of maleic acid into fumaric acid during adsorption and hydrogenation. In the polarograms given in Fig. 5 (a and b) the fumaric acid wave is absent. For comparison we give the polarogram c for an experiment on the adsorption of a mixture of maleic and fumaric acids. Table 1 gives results on the adsorption and hydrogenation of maleic and fumaric acids and also on their adsorption in admixture with succinic acid. The hydrogenation experiments were carried on until the amount of hydrogen absorbed was that which would have been required for the hydrogenation of the substance adsorbed in a parallel experiment on adsorption. It will be seen from these results that maleic acid is adsorbed somewhat better than fumaric acid, but is hydrogenated much more rapidly. Addition of succinic acid has an effect on the extents to which maleic and fumaric acids are adsorbed. We may point out that according to the literature maleic acid is adsorbed better than fumaric acid on platinum from aqueous and ethereal solutions [1] and on palladized charcoal from aqueous solutions [10]; on charcoal from aqueous and methanolic solutions, the adsorption of fumaric acid is the greater. Maleic acid is adsorbed preferentially on charcoal from its solution in 95% alcohol [11, 12].

Let us calculate the rate of hydrogenation of maleic acid, taking account of its surface concentration at the start of reaction. Let a_m be the amount of maleic acid hydrogenated in time t , and let a_f be the amount of fumaric acid hydrogenated in time t . Let a'_m and a'_f be the respective amounts of maleic and fumaric acids adsorbed on the catalyst in the standard time. Let s be the surface area of the catalyst, then $\frac{a'_m}{s} = c_s^{(m)}$ (surface concentration of maleic acid) Similarly, for fumaric acid we have:

$$\frac{a'_f}{s} = c_s^{(f)}.$$

In time t all the adsorbed substance will be completely hydrogenated, and the rate of hydrogenation of maleic acid (per unit time per unit surface area) will be:

$$v'_m = \frac{a'_m}{s \cdot t}$$

Similarly, for fumaric acid:

$$v'_f = \frac{a'_f}{s \cdot t_1} \quad (1)$$

The rates, without such consideration of surface concentrations, would be expressed as

$$v_m = \frac{a_m}{\gamma \cdot t} \quad \text{and} \quad v_f = \frac{a_f}{\gamma \cdot t_1} \quad (2)$$

in which γ is the volume of solution (ml).

Calculation of the results by Equation (1) and (2) gives the following:

$$\begin{aligned} c_s^{(m)} &= 0.00271 \text{ g/sq.m} & v'_f &= 4.7 \cdot 10^{-5} \text{ g/sq.m-second} \\ v'_m &= 15 \cdot 10^{-5} \text{ g/sq.m-second} & v_m &= 5.9 \cdot 10^{-5} \text{ g/ml-second} \\ c_s^{(f)} &= 0.0021 \text{ g/sq.m} & v_f &= 1.8 \cdot 10^{-5} \text{ g/ml-second} \end{aligned}$$

In passing to mixtures we checked whether adsorption equilibrium was substantially attained. In parallel experiments (Nos.11 and 12a, Table 2) adsorption was from a mixture of maleic and fumaric acids, but in Experiment 11 adsorption was for 10 seconds and in Experiment 12a it was for 20 seconds. The fact that the amount of substance adsorbed was unchanged indicates that the time which we selected was sufficient for the practical establishment of adsorption equilibrium.

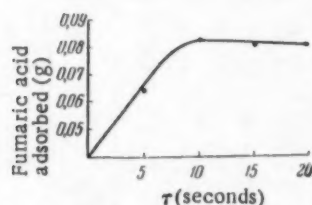


Fig. 4. Determination of the time required for the attainment of adsorption equilibrium; $c_0 = 0.185$ mole/liter; $t = 19^\circ$; $p = 1$ atm.

In the earlier experiments with the individual acids we took no account of the amount of solution remaining on the catalyst and porous plate as a result of capillary wetting forces; in the withdrawal of the solution only a small amount could be lost and, with our roughly constant concentrations, the resulting error is small and constant. In the experiments with mixtures it was necessary to take account of the amount of solution remaining on the catalyst and porous plate, because this

solution has a different ratio of components from that which would be established on the catalyst at adsorption

TABLE 2

Data on the Adsorption and Hydrogenation of the Acids in Mixtures

Experiment No.	Original amt. of maleic acid $a_0^{(m)}$ in g	Original amt. of fumaric acid $a_0^{(f)}$ in g	$\alpha_0 = \frac{a_0^{(m)}}{a_0^{(f)}}$	Amount of maleic acid adsorbed a_m , in g	Amount of fumaric acid adsorbed, a_f , in g	$\alpha_{ads} = \frac{a_m}{a_f}$	Amt. maleic acid hydrogenated a_m , in g	Amt. fumaric acid hydrogenated a_f , in g	$\alpha_h = \frac{a_m}{a_f}$	Duration of hydrogenation (sec)
8,9	0,3555	0,1590	2,236	0,0317	0,0836	0,378	0,1921	0,0457	4,206	180
9,10	0,1777	0,3188	0,558	0,0332	0,1502	0,221	0,1635	0,2033	0,804	250
11,12	0,3555	0,3181	1,117	0,0319	0,1520	0,207	0,2372	0,1283	1,857	390
12 a	0,3555	0,3181	1,117	0,0324	0,1533					
14 15	0,4899	0,3222	1,548	0,0697	0,1575	0,442	0,3670	0,1021	3,590	180

equilibrium. This amount was determined by the change in volume of solvent after passage through the porous filter (dried in an atmosphere of hydrogen) together with the standard amount of catalyst. The volume of solution required for the wetting of the catalyst and plate was found to be less than 0.25 ml, which is 1% of the volume

used in the experiments. The appropriate correction was made in the amounts of acids adsorbed, and there was a resultant change of up to 5% in the ratio of the amounts of maleic and fumaric acids adsorbed.

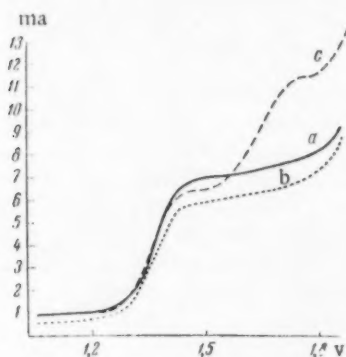


Fig. 5. Polarograms: a) experiment on adsorption of maleic acid (fumaric wave is absent); b) experiment on the hydrogenation of maleic acid (fumaric wave is absent); c) experiment on adsorption from a mixture of maleic and fumaric acids.

Experiments on the adsorption of mixtures were carried out in the same way as in the case of the individual acids. After 20 seconds the solution was withdrawn, and its concentration was determined polarographically. We might have expected that the relationships shown in Table 1 would be preserved in experiments on mixtures, but the results were different (Table 2). As characteristics of the course of adsorption and hydrogenation processes, it was found convenient to use the following quantities: α_0 , the ratio of initial amounts of maleic and fumaric acids; α_{ads} , the ratio of maleic and fumaric acids adsorbed; and α_2 , the ratio of the amounts of maleic and fumaric acids hydrogenated. It will be seen from the data in Table 2 that, in a mixture, fumaric acid is adsorbed more readily and hydrogenated less readily than is maleic acid.

the rate of reaction referred to unit surface. If

The relations obtained enable us to calculate

$$\alpha_{ads} = \frac{a'_m}{a'_f}, \text{ in which } \frac{a'_m}{a'_f} = \frac{s_m}{s_f} \text{ and } s = s_m + s_f,$$

in which s_m and s_f are the parts of the total surface s occupied by maleic and fumaric acids respectively, then

$$s_m = \frac{s \cdot \alpha_{ads}}{1 + \alpha_{ads}} \quad \text{and} \quad s_f = \frac{s}{1 + \alpha_{ads}},$$

so that

$$v'_m = \frac{a_m (1 + \alpha_{ads})}{s \cdot \alpha_{ads} \cdot t} \quad \text{and} \quad v'_f = \frac{a_f (1 + \alpha_{ads})}{s \cdot t}. \quad (3)$$

The "bulk" rates are expressed as follows:

$$v_m = \frac{a_m}{\gamma \cdot t}; \quad v_f = \frac{a_f}{\gamma \cdot t} \quad (4)$$

Quantities calculated from the results by Equations (3) and (4) are given in Table 3.

It follows from our experiments, therefore, that over a wide range of concentrations of maleic and fumaric acids in the mixtures their rates of hydrogenation, calculated on the basis of the initial surface concentrations of the acids, change very little. This indicates that, over the range of concentrations taken, the catalyst surface is saturated both with maleic acid and with fumaric acid. However, with increase in the concentration of maleic acid the extent of adsorption increased, though the rate of hydrogenation scarcely changed (Experiments 14 and 15).

The results obtained without the use of kinetic curves and treated by the method discussed above so as to give the mean rate of hydrogenation per unit surface show that measurements of only bulk rates can give qualitatively different results (Experiments 9 and 10). It is interesting that the rate calculated per unit surface is

less for the individual acids than for their hydrogenation in a mixture. The observed higher rate of hydrogenation of maleic acid, as compared with fumaric acid, is in accord with the geometric requirements of the multiplet



Fig. 6. Orientation of the acids on the catalyst surface; a) a flat orientation is possible both for the cis- and for the trans-acid; b) an edgewise orientation is possible only for the cis-acid.

theory, because cis-substituted olefins can lie both flat and edgewise on the catalyst surface (Fig. 6), whereas trans-substituted olefins can lie only flat. At the same time we must not forget energy factors, which are also considered in the multiplet theory.

Lebedev [13] supposed that the higher rate of hydrogenation of one compound, as compared with that of another, was to be attributed to its greater adsorption. The direct experiments of Platonov [1] on the adsorption of maleic and fumaric acids on platinum black appeared to give experimental support to this view. However, as will be seen from present investigation, until now the

difference between surface and bulk concentrations has not been taken into account in catalysis.

TABLE 3
Speed of Hydrogenation of Maleic and Fumaric Acid in Mixtures

Experiment	Rates of hydrogenation, calculated on the basis of surface concentration ($\times 10^{-5}$ g/sq.m · second)		*Bulk* rates of hydrogenation ($\times 10^{-5}$ g/ml · second)	
	for maleic acid	for fumaric acid	for maleic acid	for fumaric acid
8.9	9.4	0.84	4.1	0.97
9.10	9.0	2.5	2.6	3.2
11.12	8.7	0.99	2.4	1.3
14.15	13	2.0	8.0	2.3

Actually, several types of adsorption must be distinguished. In the molecular adsorption of maleic and fumaric acids, the molecules are probably oriented with their carboxyl groups toward the metal catalyst, and here the dipole moment also plays a part. Only after this process does the chemisorption of the olefin bond, which is necessary for catalysis, begin to take place. Here it is necessary to take account also of the heterogeneity of the catalyst surface. These complicated relationships provide the explanation of the absence of a strict parallelism between the adsorption and catalysis of maleic and fumaric acids.

SUMMARY

1. A procedure for the study of liquid-phase catalytic hydrogenation is described. Suitable apparatus has been devised, and a method is proposed for the determination of surface concentrations in the hydrogenation process.
2. It was shown that, in 96% alcohol over Raney nickel, maleic acid is adsorbed and hydrogenated more readily than fumaric acid. Succinic acid has a displacing action on maleic and fumaric acids. In a mixture of acids in 96% alcohol over Raney nickel, fumaric acid is adsorbed more readily than maleic acid, but is hydrogenated more slowly.
3. In the study of catalytic-hydrogenation processes in a mixture, it is necessary to take into account the surface concentrations of the reactants at the moment of reaction.

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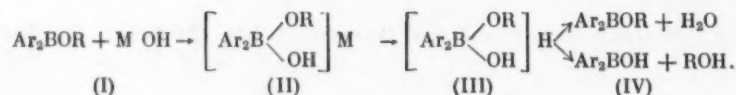
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ORGANOBORON COMPOUNDS

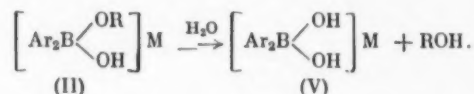
COMMUNICATION 22. MECHANISM OF THE HYDROLYSIS OF DIARYLBORINIC ESTERS

B. M. Mikhailov and V. A. Vaver

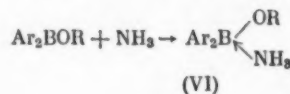
Alkyl diarylborinates, unlike areneboronic esters, are stable to the action of such hydrolyzing agents as acids and alkali-metal hydroxides [1, 2]. Under the action of these agents diarylborinic esters (I) dissolve with formation of salts of alkoxydiarylhydroxyboric acids (II). On acidification of the solution these salts are converted only to a slight extent into diarylborinic acids (IV); for the main part the intermediately formed alkoxydiarylhydroxyboric acids (III) suffer elimination of water, not alcohol, and are reconverted into the original ester:



The hydrolysis of diarylborinic esters with caustic alkalis has been brought about only in a few cases, and then only by heating salts of alkoxydiarylhydroxyboric acids (II) in aqueous solution. Under these conditions replacement of alkoxy by hydroxyl in the complex anion of the salt (II) can occur with formation of salts of diaryldihydroxyboric acids (V), which form the acids when the solution is acidified:



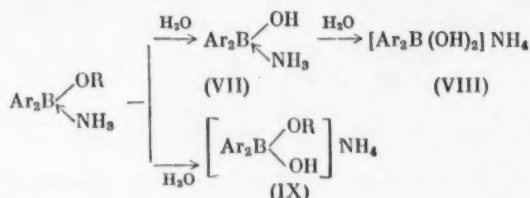
The hydrolysis of diarylborinic esters proceeds extremely readily under the action of aqueous solutions of ammonia or barium hydroxide [1, 2]. In a previous paper [1] we proposed a mechanism for the hydrolysis of diarylborinic esters with aqueous ammonia solution which included as its first stage the formation of ammines of diarylborinic esters (VI), which are then hydrolyzed:



This suggestion was based on the fact that the hydrolysis of diarylborinic esters with aqueous ammonia, unlike hydrolysis with caustic alkalis, proceeds extremely readily, being complete in a few minutes at room temperature. It is clear that this reaction cannot proceed through the stage of formation of ammonium alkoxydiarylhydroxyborate [(II), M = NH₄], because it is difficult to see why the ammonium salts of alkoxydiarylhydroxyboric acids should be readily hydrolyzed, when the analogous sodium and potassium salts are stable in aqueous solution. The further transformations of ammines of diarylborinic esters (VI) under the action of water evidently consist in the replacement of alkoxy by hydroxyl and the formation of ammines of diarylborinic acids (VII), which are then converted into ammonium salts of diaryldihydroxyboric acids.

Another way in which the ammonium salts (VIII) might be formed from the ammines (VI), consisting in the

displacement of ammonia into the outer spheres of the complex with formation of ammonium alkoxydiarylhydroxyborates (IX), is excluded, because the latter compounds do not hydrolyze in aqueous solution.



In order to provide proof of the proposed mechanism of hydrolysis, we prepared amines of various diarylborinic esters and investigated their behavior toward water. The amines were prepared by the passage of dry gaseous ammonia through isopentane or petroleum ether solutions of diarylborinic esters. In this we prepared the amines of propyl, butyl, isobutyl, and isopentyl diphenylborinates, or isobutyl bis-*p*-chlorophenylborinate, or isobutyl bis-*p*-bromophenylborinate, and also of the previously undescribed isobutyl esters of di-*p*-tolyl- and di-*o*-tolyl-borinic acids.

With only one exception, these amines of diarylborinic esters were found to be extremely reactive toward water: when shaken with water at room temperature they are rapidly converted into salts of diaryldihydroxyboric acids, which give diarylborinic acids on acidification. The conversion of the amines of the esters into ammonium diaryldihydroxyborates under the action of water confirms the proposed mechanism for the hydrolysis of diarylborinic esters with aqueous ammonia.

Of the amines enumerated above, only that formed from isobutyl bis-*p*-chlorophenylborinate was found to be stable toward water. Without going into the causes of the unexpected stability of this ammine, we may note that this case again confirms the proposed mechanism, because the original isobutyl bis-*p*-tolylborinate does not react with aqueous ammonia and does not form ammonium bis-*p*-chlorophenyldihydroxyborate.

Ammonium diaryldihydroxyborates were prepared both by hydrolysis of the corresponding amines and directly from diarylborinic esters. Acidification of solutions of ammonium dihydroxydi-*p*-tolyl- and dihydroxydi-*o*-tolyl-borates gave the previously undescribed di-*p*-tolyl- and di-*o*-tolyl-borinic acids. By the transesterification of the isobutyl esters of these two acids with 2-aminoethanol we prepared the 2-aminoethyl esters of di-*p*-tolyl- and di-*o*-tolylborinic acids. These esters, like the 2-aminoethyl esters of other diarylborinic acids described previously by Letsinger and co-workers [3, 4], are crystalline substances, stable in the air and satisfactory for use in the characterization of di-*o*-tolyl- and di-*p*-tolylborinic acids.

EXPERIMENTAL

Butyl Diphenylborinate. Butyl diphenylborinate was synthesized under the same conditions as those described previously for the synthesis of isobutyl diphenylborinate [1]. At temperatures ranging from -30° to -50° , a solution of 103 g (0.45 mole) of tributyl borate in 200 ml of dry ether was added to a solution of 1 mole of phenylmagnesium bromide, prepared from 24.4 g of magnesium and 154 g of bromobenzene in 800 ml of dry ether. The reaction mixture was stirred for ten hours at -75° , and the reaction products were then treated with 700 ml of 5% hydrochloric acid. The benzeneboronic acid present in the mixture after the hydrolysis was esterified with butyl alcohol, and the product was vacuum-fractionated in a stream of dry nitrogen. The following fractions were collected:

Fraction I, b.p. $95-108^\circ$ (1.5 mm), 4.2 g	
Fraction II, b.p. $108-110^\circ$ (1.5 mm); 22.0 g	
Fraction III, b.p. $110-120^\circ$ (1.0 mm); 9.2 g	
Fraction IV, b.p. $120-120.5^\circ$ (1.0 mm); 50.0 g	
Residue	10.3 g

Fraction III (d_4^{20} 0.9834; n_D^{20} 1.5471) was butyl diphenylborinate.

Found %: C₆H₅ 64.78; B 4.57. (C₆H₅)₂BOC₄H₉. Calculated %: C₆H₅ 64.79; B 4.54.

The yield of butyl diphenylborinate was 46.7%. Fraction II (d^{20}_4 0.9292) was dibutyl benzeneborate, for which the literature [5] gives b.p. 139-140° (10 mm) and d^{25}_4 0.9166.

Isopentyl Diphenylborinate. Reaction was between 0.7 mole of phenylmagnesium bromide in 600 ml of dry ether and 85 g (0.31 mole) of triisopentyl borate in 100 ml of dry ether. The synthesis and the treatment of the reaction products were carried out as described for isobutyl and butyl diphenylborinates, with the difference that the ester and the isopentyl alcohol formed after hydrolysis of the reaction products were removed in a vacuum at a bath temperature not exceeding 60°. Vacuum fractionation in a stream of dry nitrogen gave 32.8 g (42%) of isopentyl diphenylborinate; b.p. 128-129° (2 mm); d^{20}_4 0.9710, n^{20}_D 1.5405.

Found %: C_6H_5 61.10; B 4.21. $(C_6H_5)_2BOC_5H_{11}$. Calculated %: C_6H_5 61.15; B 4.29.

The residue remaining after the separation of isopentyl diphenylborinate was esterified with 30 ml of isopentyl alcohol. After removal of excess of alcohol and vacuum fractionation we isolated 35.5 g (43.5%) of diisopentyl benzeneborinate, b.p. 116-117° (2 mm); d^{20}_4 0.9221.

Found %: C_6H_5 29.55; B 4.05. $(C_6H_5)_2B(OC_5H_{11})_2$. Calculated %: C_6H_5 29.23; B 4.10.

Propyl Diphenylborinate. From 0.5 mole of phenylmagnesium bromide and 0.22 mole of tripropyl borate, by the same procedure we obtained 13.46 g (27%) of propyl diphenylborinate; b.p. 125-126° (5 mm); d^{20}_4 0.9851; n^{20}_D 1.5491.

Found %: C_6H_5 68.71; B 4.80. $(C_6H_5)_2BOC_3H_7$. Calculated %: C_6H_5 68.81; B 4.83.

From the residue, after treatment with isopentane, we obtained 11.1 g (48.5%) of benzeneboronic anhydride, m.p. 187-189°.

All the diphenylborinic esters obtained are colorless viscous liquids which are miscible in all proportions with most organic solvents; when cooled to temperature of from -40° to -50°, they freeze into a glassy mass; they are slowly oxidized in the air. Benzeneboronic esters are colorless mobile liquids, which mix with most organic solvents and are rapidly hydrolyzed in moist air with formation of benzeneboronic acid.

Isobutyl Di-p-tolylborinate. At temperatures ranging from -30° to -60° a solution of 53 g (0.23 mole) of triisobutyl borate in 150 ml of dry ether was added to an ethereal solution of p-tolylmagnesium bromide prepared from 86.0 g (0.505 mole) of p-bromotoluene and 12.30 g of magnesium in 500 ml of ether. The synthesis and treatment of the reaction products were carried out as described for isobutyl diphenylborinate. Vacuum fractionation of the reaction products in a stream of dry nitrogen gave 12.0 g (19.6%) of isobutyl di-p-tolylborinate; b.p. 146-146.5° (2.5 mm); d^{20}_4 0.9630; n^{20}_D 1.5448.

Found %: $CH_3C_6H_4$ 68.05; B 4.14. $(CH_3C_6H_4)_2BOC_4H_9$. Calculated %: $CH_3C_6H_4$ 68.47; B 4.05.

Apart from the di-p-tolylborinic ester, by hydrolysis of the fraction of b.p. up to 146° (2.5 mm) we isolated 8.80 g (30%) of p-tolueneboronic acid, m.p. 227-230°, and 1.7 g of bi-p-tolyl, m.p. 119-121°. As a result of the further fractionation of reaction products boiling above 146.5° (2.5 mm) we isolated 7.3 g of tri-p-tolylborine, b.p. 230-235° (12 mm) [6].

Isobutyl Di-o-tolylborinate. A solution of 0.22 mole of triisobutyl borate in 100 ml of dry ether was cooled to -70° and was stirred for four hours while a solution of 0.5 mole of o-tolylmagnesium bromide in 300 ml of ether was added. The reaction mixture was stirred for six hours at -70° and was left overnight in the cooling bath. After the usual treatment and vacuum fractionation we obtained 5.1 g of isobutyl di-o-tolylborinate; b.p. 135° (1.2 mm); d^{20}_4 0.9704; n^{20}_D 1.5440.

Found %: $CH_3C_6H_4$ 68.34; B 4.06. $(CH_3C_6H_4)_2BOC_4H_9$. Calculated %: $CH_3C_6H_4$ 68.47; B 4.06.

From the reaction products we isolated also 30.5 g (55%) of diisobutyl o-tolueneboronate, b.p. 110-112° (3 mm), and 9.8 g (16.3%) of tri-o-tolylborine, b.p. 182-184° (2 mm) [6]. Di-p-tolyl- and di-o-tolyl-borinic esters are colorless liquids, which oxidize slowly in the air and are miscible in all proportions with organic solvents.

Ammines of Diarylborinic Esters. For the preparation of ammines a solution of 1-2 g of the diarylborinic ester in dry isopentane or petroleum ether was saturated with dry gaseous ammonia (10-15 minutes). The ammines were filtered off, washed with isopentane or petroleum ether, and vacuum-dried.

Ammonium Dihydroxydi-p-tolylborate. Isobutyl di-p-tolylborinate (0.66 g) was added to 5.0 ml of 30% ammonia solution. The mixture was shaken for ten minutes, and the salt was filtered off, washed with water, vacuum-dried, and recrystallized from dry benzene. Yield 0.53 g (86.17%); m.p. 89-91° (in a sealed capillary); colorless leaves, insoluble in water, but readily soluble in methanol and ethanol.

Found %: N 5.72. $C_{14}H_{20}BO_2N$. Calculated %: N 5.72.

TABLE 1

Preparation and Properties of Ammines of Diarylborinic Esters

Formula of original ester	Solvent	Yield of ammine (%)	M.p. of ammine (°C)
$(C_6H_5)_2B(O-n-C_3H_7)$	Petroleum ether	97,5	104-107
$(C_6H_5)_2B(O-n-C_4H_9)$		90,3	97-99
$(C_6H_5)_2B(O-i-C_4H_9)$	Isopentane	88,4	103-105
$(C_6H_5)_2B(O-i-C_5H_{11})$	Petroleum ether	95,3	99-101
$(n-C_6H_{13})_2B(O-i-C_4H_9)$	"	92,4	115-117
$(p-BC_6H_4)_2B(O-i-C_4H_9)$	"	92,0	113-115
$(p-CH_3C_6H_4)_2B(O-i-C_4H_9)$	"	84,7	77-79
$(o-CH_3C_6H_4)_2B(O-i-C_4H_9)$	Isopentane	80,0	88-90,5*

* The melting point was determined in a sealed capillary.

Ammonium Dihydroxydi-o-tolylborate. Isobutyl di-o-tolylborinate (0.68 g) was treated with 5.0 ml of 10% aqueous ammonia. The ammonium salt was filtered off, washed with water, carefully pressed out on the filter, washed with ether, and vacuum-dried. The product, amounting to 0.56 g (89.5%), was ammonium dihydroxydi-o-tolylborate, m.p. 97-100° (in a sealed capillary). The substance is readily soluble in alcohols, sparingly soluble in ether, and insoluble in water. When an attempt was made to recrystallize the salt from benzene, partial decomposition occurred.

Found %: N 5.69. $C_{14}H_{20}BO_2N$. Calculated %: N 5.72.

Hydrolysis of Ammines of Diarylborinic Esters. The ammine of isobutyl diphenylborinate (0.74 g, i.e., 0.003 mole) was treated with water (2.5 ml) at room temperature. The reaction product was filtered off, vacuum-dried at 35°, and recrystallized from benzene. The product, amounting to 0.56 (89%), was ammonium dihydroxydiphenylborate [1], m.p. 108-110°. A mixture with an analyzed sample of ammonium dihydroxydiphenylborate melted at 108-110°. Hydrolysis with water with formation of the corresponding diaryldihydroxyborates occurred also with the ammines of propyl, butyl, and isopentyl diphenylborinates and of isobutyl bis-p-bromophenyl-, dip-p-tolyl- and di-o-tolylborinates. The ammine of isobutyl bis-p-chlorophenylborinate was not hydrolyzed by water.

Di-p-tolylborinic Acid. To a suspension of 1.67 g of ammonium dihydroxydi-p-tolylborate in 10 ml of ether, 10 ml of dilute (1 : 2) hydrochloric acid was added. The mixture was shaken for five minutes, the ether layer was separated, and the solution was extracted with ether. The ethereal solution was evaporated at 15-20 mm at 60° for ten minutes. When cool, the contents of the flask solidified completely. The reaction product was washed with a little low-boiling petroleum ether. The yield of di-p-tolylborinic acid, m.p. 64-65.5°, was 1.25 g (88%). After recrystallization from petroleum ether it melted at 65-66°; fine colorless crystals, highly soluble in most organic solvents, but sparingly soluble in isopentane and low-boiling petroleum ether.

Found %: C 80.94; H 7.20; B 5.42. $C_{14}H_{15}BO$. Calculated %: C 80.04; H 7.20; B 5.15.

Di-o-tolylborinic Acid. In a similar manner, 1.52 g of ammonium dihydroxydi-o-tolylborate was treated with 10 ml of dilute (1 : 2) hydrochloric acid. Ether was removed from the ether extract, and the residue was heated for ten minutes at 60° (15-20 mm), cooled, and diluted with isopentane. The yield of di-o-tolylborinic acid was 1.20 g (92.5%). It was obtained as well-formed rectangular plates, m.p. 64-66°, readily soluble in most organic

solvents, but sparingly soluble in isopentane.

Found %: C 80.07; H 7.26; B 5.15. $C_{14}H_{15}BO$. Calculated %: C 80.04; H 7.20; B 5.15.

2-Aminoethyl Di-p-tolyl- and Di-o-tolyl-borinates. A solution of 0.5 g of isobutyl di-p-tolylborinate in a mixture of 10 ml of alcohol and 2 ml of water was mixed with 0.2 g of 2-aminoethanol. A yield of 0.44 g of 2-aminoethyl di-p-tolylborinate, m.p. 174-176°, was obtained (crystallizes in leaves from alcohol).

Found %: N 5.69. $C_{16}H_{20}BON$. Calculated %: N 5.53.

Similar reaction between 0.4 g of isobutyl di-o-tolylborinate and 0.2 g of 2-aminoethanol gave 0.35 g of 2-aminoethyl di-o-tolylborinate. This crystallized from alcohol in needles, m.p. 179-180.5°.

Found %: N 5.65. $C_{16}H_{20}BON$. Calculated %: N 5.53.

The synthesis of diarylborinic esters was carried out in an atmosphere of nitrogen. Boron and aryl groups were determined by the method proposed by Witting and co-workers [7].

SUMMARY

1. Hydrolysis of diarylborinic esters with aqueous ammonia solution passes through the intermediate formation of amines of diarylborinic esters with their subsequent conversion into ammonium diaryldihydroxyborates.
2. Various diarylborinic esters and their amines were synthesized.
3. Previously undescribed di-o-tolyl- and di-p-tolyl-borinic acids and their derivatives were prepared.

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REACTIONS OF FLUORO OLEFINS

COMMUNICATION 2. PREPARATION AND SOME PROPERTIES OF PENTAFLUORO-2-IODOPROPENE

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Until recently, the only completely halogenated olefins known in which a halogen atom other than fluorine is attached to a carbon atom bound to its neighbor by a multiple bond were chloro and bromo olefins. Among similar iodine derivatives, the properties of which are of undoubted interest, only trifluoriodoethylene has been described [1].

The simplest method of preparing the second member of the series of perfluorovinyl iodides, pentafluoro-2-iodopropene, would appear to be the dehydrohalogenation of 1-chloro-1,1,3,3,3-pentafluoro-2-iodopropane, which in its turn might be prepared by reaction of 1,1,3,3,3-pentafluoropropene with iodine chloride. It was, in fact, found that heating of $\text{CF}_3\text{CH}=\text{CF}_2$ with a small excess of ICl at $100-120^\circ$ for ten hours gave a 56% yield of 1-chloro-1,1,3,3,3-pentafluoro-2-iodopropane, which is a heavy liquid, b.p. $94-96^\circ$. In addition to $\text{CF}_3\text{CHICF}_2\text{Cl}$, small amounts of 1,2-dichloro-1,1,3,3,3-pentafluoropropane were also isolated. The direction of the addition of iodine chloride to 1,1,3,3,3-pentafluoropropene was proved by the fact that dehydrohalogenation of the product with aqueous NaOH solution gave a 71% yield of pentafluoro-2-iodopropene, a heavy liquid of b.p. $51-53^\circ$. It is quite obvious that the other order of addition of iodine chloride to 1,1,3,3,3-pentafluoropropene could not yield pentafluoro-2-iodopropene.

From an examination of work on the addition of alcohols to fluoro olefins [2-6] we may conclude that, with increase in the polarity of the latter, the readiness with which addition of alcohols occurs increases. It is true that no quantitative results characterizing this tendency have been reported. Pentafluoro-2-iodopropene was found to be the most polar of the known perfluorovinyl halides; its dipole moment is 1.54 D. But even such a comparatively high polarity was found to be insufficient for addition of alcohol to occur in absence of catalyst. Addition of methanol to pentafluoro-2-iodopropene was brought about by heating the mixture in an autoclave in presence of triethylamine, and a 61% yield of $\text{CH}_3\text{OCF}_2\text{CHICF}_3$ was obtained; it is a pleasantly smelling colorless liquid, b.p. 53° (55 mm). This ether is of some interest in that it can serve as starting material for the preparation of 3,3-difluoroacrylic esters.

By heating $\text{CF}_3\text{CHICF}_2\text{OCH}_3$ with 96% sulfuric acid we obtained in 70% yield the previously undescribed methyl 3,3,3-trifluoro-2-iodopropionate as a pleasantly smelling liquid of b.p. $70-73^\circ$ (40 mm). Dehalogenation of this ester with zinc in a diisopentyl ether medium at $150-170^\circ$ gave methyl 3,3-difluoroacrylate, which has been synthesized previously by a different method [7].

EXPERIMENTAL

Reaction of 1,1,3,3,3-Pentafluoropropene with Iodine Chloride. Iodine chloride (41 g, i.e., 0.25 mole) was introduced into a 70-ml stainless steel test tube; the test tube was cooled to -60° , 30 g (0.23 mole) of liquid 1,1,3,3,3-pentafluoropropene was added, and the reaction mixture was heated in a rotating autoclave for ten hours at $100-120^\circ$. The test tube was then cooled to -60° , and unchanged olefin was collected in a calibrated gas holder (0.5 liter). The reaction product, a dark-violet liquid, was washed several times with sodium thiosulfate solution and with water and was then dried over magnesium sulfate. Distillation gave Fraction I (4 g, b.p. 50° , which consisted of 1,2-dichloro-1,1,3,3,3-pentafluoropropane, and Fraction II (38 g, i.e., 56%), b.p. $94-96^\circ$, which consisted of 1-chloro-1,1,3,3,3-pentafluoro-2-iodopropane; d_{20}^{20} 2.1142; n_D^{20} 1.3940; found MR 33.60; calculated

MR 33.72; found Cl + I 55.20%; F 32.00%; calculated for C_3HF_5ClI : Cl + I 55.5%; F 32.30%; found M 290; calculated for C_3HF_5ClI M 294.

Preparation of Pentafluoro-2-iodopropene. A three-necked flask fitted with stirrer, fractionating column, and dropping funnel was charged with 50 g of 50% aqueous KOH (or NaOH) solution. The alkali was heated to 80°, and 43 g (0.14 mole) of 1-chloro-1,1,3,3,3-pentafluoro-2-iodopropane was added dropwise from the funnel. The pentafluoro-2-iodopropene that distilled off was collected in a receiver cooled to -20°; it was washed with water and dried over magnesium sulfate. The yield of crude product was 29 g, and fractionation of this gave 22 g of a substance of b.p. 51-53°; a 71% yield of pentafluoro-2-iodopropene; d_{20}^{20} 2.0931; n_D^{20} 1.3710; found MR 28.51; calculated MR 28.59; found I 49.90%; F 36.30%; calculated for C_3F_5I : I 49.30%; F 36.82%; found M 252; calculated for C_3F_5I : M 258.

Addition of Methanol to Pentafluoro-2-iodopropene. A mixture of 32 g (1 mole) of absolute methanol, 3.0 g of triethylamine, and 25 g of pentafluoro-2-iodopropene was prepared in a 25-ml stainless steel test tube. The tube was closed, and the reaction mixture was heated in a rotating autoclave for 7-8 hours at 60-70°. The tube was then cooled to -29° and opened. The reaction product was washed with ice water, dried over magnesium sulfate, and vacuum-distilled. The product amounting to 16 g (61%), was 1,1,3,3,3-pentafluoro-2-iodopropyl methyl ether, b.p. 53° (55 mm); d_{20}^{20} 2.0207; n_D^{20} 1.4120; found MR 36.05; calculated MR 35.24.

When sodium methoxide was used instead of triethylamine the yield was reduced to 30%.

Hydrolysis of 1,1,3,3,3-Pentafluoro-2-iodopropyl Methyl Ether. A three-necked flask fitted with stirrer, dropping funnel, and thermometer was charged with 5 ml of 96% sulfuric acid and 1 g of glass powder. The flask was heated to 70°, and 15 g (0.052 mole) of 1,1,3,3,3-pentafluoro-2-iodopropyl methyl ether was added dropwise from the funnel over a period of one hour. The reaction mixture was poured into ice water, the precipitated oil was separated, and the aqueous layer was extracted with ether. The ether extract was combined with the oil and dried over magnesium sulfate. Ether was distilled off, and 9.5 g (70%) was obtained of a fraction of b.p. 70-73° (40 mm); this was methyl 3,3,3-trifluoro-2-iodopropionate $CF_3CHICOOCH_3$; d_{20}^{20} 1.9846; n_D^{20} 1.4350; found MR 35.06; calculated MR 35.26; found I 47.12%; F 21.60%; calculated for $C_4H_4O_2F_3I$: I 47.45%; F 21.30%; found M 261; calculated for $C_4H_4O_2F_3I$: M 268.

Preparation of Methyl 3,3,-Difluoroacrylate. A mixture of 5 ml of diisopentyl ether and 2 g of activated zinc dust was prepared in a three-necked flask fitted with stirrer, dropping funnel, and fractionating column. The flask was heated to 150-170°, and with vigorous stirring 4.5 g (0.0185 mole) of methyl 3,3,3-trifluoro-2-iodopropionate was slowly added dropwise from the funnel. The substance that distilled over was collected in an ampoule cooled with ice water; it was distilled and gave a fraction of b.p. 91-93° (0.6 g, i.e., 29%) consisting of methyl 3,3-difluoroacrylate; d_{20}^{20} 1.1993; n_D^{20} 1.3375; found MR 21.06; calculated MR 21.67; found C 38.87%; H 3.52%; calculated for $C_4H_4O_2F_2$: C 39.34%; H 3.27%; found M 114; calculated for $C_4H_4O_2F_2$: M 122. $CH_3OCOCH=CF_2$ is a pungently smelling colorless liquid which readily decolorizes bromine water.

SUMMARY

1. Pentafluoro-2-iodopropene was prepared by the dehydrohalogenation of 1-chloro-1,1,3,3,3-pentafluoro-2-iodopropane.
2. By addition of methanol to pentafluoro-2-iodopropene, previously undescribed 1,1,3,3,3-pentafluoro-2-iodopropyl methyl ether was prepared.
3. By the hydrolysis of this ester, methyl 3,3,3-trifluoro-2-iodopropionate was synthesized, and dehalogenation of this gave methyl 3,3-difluoroacrylate.

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OXIDE-METAL CATALYSTS FOR THE REFORMING OF GASOLINES

COMMUNICATION 3. TRANSFORMATIONS OF THE 89.5-126° FRACTION OF GASOLINE FROM SECOND BAKU PETROLEUMS OVER A PALLADIUM CATALYST

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and I. N. Kurdiumova

In our previous communications [1, 2] we have presented experimental data obtained in the study of the transformations of gasoline fractions of certain petroleum over platinum catalysts. In these papers we made a detailed examination of the individual parameters of the process (temperature, pressure, space velocity, and ratio of recycled gas to original material) as they affect the yield of aromatic hydrocarbons and the activity and stability of the catalysts. We also studied the effect of the chemical nature of the carrier on the activity and stability of the catalyst under the conditions of the reforming of the 85-138° fraction of the gasoline of Second Baku petroleum; it was then shown that a 0.5% Pt-Al₂O₃ catalyst has considerable advantages (high yield of aromatic hydrocarbons and less gas formation) over a 0.5% Pt-SiO₂ catalyst.

In the present communication we give experimental material obtained in the study of the transformations of the 89.5-126° fraction of gasoline from Second Baku petroleum over two samples of palladium catalyst. The question of the use of palladium, a metal that is more readily available than platinum, for the reforming of gasolines has become particularly important in view of the increased production of gasolines refined by catalytic reforming. Moreover, in all investigations [3-9] devoted to the catalytic treatment of petroleum distillates with the aid of active and stable oxide-metal catalysts, though various carriers are used the metal employed is almost exclusively platinum.

Two of the present authors [10] have previously investigated low-percentage palladium catalysts (0.05-2.0% Pd on charcoal) and found that they possess fairly high dehydrogenating power, but rapidly become exhausted under the conditions of the transformation of gasoline fractions. Palladium catalysts (0.5% Pd on Al₂O₃ and SiO₂), prepared later by Shuikin, Minachev, and co-workers for the investigation of the transformations of ethylcyclopentane [11], heptane [12], methylcyclohexane [13], and ethylcyclohexane [14], showed not only hydrogenation and dehydrogenation properties, but also dehydrocyclization and isomerization power. However, the stabilities of these catalysts were not studied.

In recent years some patents have appeared [15-18] in which palladium catalysts of various carriers have been proposed, as well as platinum catalysts, for the catalytic reforming of gasolines. There is no information in these patents concerning the activity and stability of these catalysts. In a recent investigation [19], three of the present authors studied a catalyst containing 0.5% of palladium supported on alumina which had received a preliminary treatment with dilute hydrofluoric acid. The palladized alumina was then treated further with H₂S. The catalyst showed high activity and quite satisfactory stability in the reforming of the 98-109° fraction of straight-run gasolines of Il'sk-Khadzyzhinsk petroleum of low sulfur content (0.0025%).

As Second Baku petroleum, which, unlike Caucasian petroleum, contain appreciable amounts of sulfur, have recently acquired great importance, in the present investigation we studied the activity and stability of palladium catalysts under the conditions for the reforming of the 89.5-126° fraction of gasoline from Second Baku petroleum. At the same time, with the object of determining the parts played by the various classes of hydrocarbons in the reforming of this fraction, we made detailed analyses, both of the original gasoline and of the catalyzates, for the contents of individual hydrocarbons.

EXPERIMENTAL

Preparation of Samples of 0.5% Pd-Al₂O₃ Catalyst. Sample 1. Aluminum hydroxide was prepared by the precipitation of 1 M Al(NO₃)₃ with 12% aqueous ammonia. The resulting hydrogen was washed free from NO₃⁻ ions with distilled water, filtered off, and dried at 130-140° for 6-8 hours. The dried mass was roasted at 500° for 3-4 hours; it was ground to a powder, which was then converted into cylindrical tablets, 5 mm in diameter and 5 mm high, in a special press; the tablets were impregnated with H₂PdCl₄ solution of the necessary concentration and then dried at 110-120°.

Sample 2. This was prepared like Sample 1, except that, after being dried at 130-140° and before being roasted, the mass was treated with dilute hydrofluoric acid (calculated to give 0.5% of fluorine on the weight of Al₂O₃). The pH of the extract of Sample 2 was 6.*

Analytical Procedure. The original material and liquid catalyzates were analyzed for aromatic hydrocarbons (sulfuric acid method) and sulfur (lamp method). The compositions of these materials with respect to individual hydrocarbons were determined by the combined method [20]. Gaseous products were analyzed in an Orsat-Lunge apparatus.

Characteristics of the Original Gasoline Fraction. The 89.5-126° fraction of gasoline from Second Baku petroleum had: n_D²⁰ 1.4040 and d₄²⁰ 0.7187; content of aromatics 7.0% by volume; sulfur content 0.017% by weight.

Engler Fractionation at 741.6 mm

Start of distillation	89.5°	90%	113.0°
10%	98.0°	95%	123.0°
50%	99.5°	End of distillation	126.0°

The fraction was accounted for to the extent of 91.4% by weight; forty hydrocarbons were found, and their contents were determined quantitatively. Their distribution among the classes is shown in Table 1. The results of the analysis of the fraction are given in Table 2.

TABLE 1

Class Distribution of Hydrocarbons in the 89.5-126° Fraction

Class of hydrocarbons	Number of hydrocarbons
Paraffins	19
Cyclopentanes	9
Cyclohexanes	8
Aromatics	4

The data of Table 2 permit the establishment of the group composition of the original fraction, which is given in Table 3.

In the naphthene part of the fraction, the ratio of the contents of cyclopentane and cyclohexane hydrocarbons was 0.79. In the paraffin part, normal hydrocarbons predominated (29.3%). The branched paraffins consisted of 42.7% of hydrocarbons having a tertiary carbon atom and only 1.67% of hydrocarbons with a quaternary carbon (expressed on the total amount of paraffins). As regards paraffins of identical molecular weight, all possible C₅ and C₆ isomers were found except

2-methylbutane and 2,2-dimethylpropane, and of the C₇ hydrocarbons only 2,2,3-trimethylbutane and 3,3-dimethylpentane were absent. Of C₈ hydrocarbons we detected octane, 2- and 4-methylheptanes, 2,4-dimethylhexane, and 2,3,4-trimethylpentane. A small amount of 2,2,4-trimethylhexane (a C₉ paraffin) was also found. Among the cyclopentane hydrocarbons there was a predominance of trans-1,2-dimethylcyclopentane (7.14%), cis- and trans-1,3-dimethylcyclopentanes (3.17%), ethylcyclopentane (1.19%), and methylcyclopentane (1.18%). In the cyclohexane group the first place was occupied by methylcyclohexane (11.37%), whereas the content of cyclohexane was only 3%. Of the dimethylcyclohexanes, 1,3-dimethylcyclohexane predominated. In the fraction we found also 1,1,3-trimethylcyclohexane, a hydrocarbon containing a quaternary carbon atom. The aromatic hydrocarbons fell in the following order of diminishing content in the fraction: toluene, m-xylene, benzene, and o-xylene.

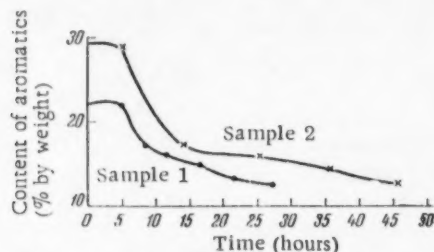
* A 2.00-g sample of the catalyst was boiled in 80 ml of doubly distilled water for one hour. The contents of the flask were then transferred to a 200-ml measuring flask and made up to volume with doubly distilled water. The pH of the filtered extract was determined with an LP-5 electron-tube potentiometer.

TABLE 2

Individual Hydrocarbons in the 89.5-126.0° Fraction

Hydrocarbon	Content (% by weight)	Hydrocarbon	Content (% by weight)
Paraffins			
Pentane	0.42	2-Methylhexane	4.62
Hexane	3.95	3-Methylhexane	5.23
2-Methylpentane	0.65	3-Ethylpentane	0.13
3-Methylpentane	1.01	Octane	4.33
2,2-Dimethylbutane	0.52	2,4-Dimethylhexane	0.75
2,3-Dimethylbutane	0.11	2-Methylheptane	3.68
Heptane	20.59	4-Methylheptane	3.03
2,2-Dimethylpentane	0.22	2,3,4-Trimethylpentane	0.75
2,3-Dimethylpentane	2.30		
2,4-Dimethylpentane	0.30	2,2,4-Trimethylhexane	0.14
		Total	52.7
Cyclopentane Hydrocarbons			
Methylcyclopentane	1.18	1,2-Dimethylcyclopentane (cis)	0.15
1,1-Dimethylcyclopentane	0.39	Ethylcyclopentane	1.19
1,3-Dimethylcyclopentane (trans)	1.82	1,2,3-Trimethylcyclopentane (cis-trans-cis)	1.01
1,3-Dimethylcyclopentane (cis)	1.35	1,1,3-Trimethylcyclopentane	0.37
1,2-Dimethylcyclopentane (trans)	7.14		
		Total	14.6
Cyclohexane Hydrocarbons			
Cyclohexane	3.07	1,2-Dimethylcyclohexane	0.14
Methylcyclohexane	11.34	1,3-Dimethylcyclohexane	1.46
Ethylcyclohexane	0.68	1,4-Dimethylcyclohexane	0.64
1,1-Dimethylcyclohexane	0.07	1,1,3-Trimethylcyclohexane	1.08
		Total	18.5
Aromatics			
Benzene	0.47	m-Xylene	0.50
Toluene	4.46	o-Xylene	0.21
		Total	5.6
		Accounted for (% on original fraction)	91.4
		Residue in flask after fractionation (%)	2.5
		Losses (%)	6.1
		Total	100.0

Experimental Conditions. The experiments on the reforming of the 89.5-126° fraction were carried out in a flow-type apparatus with gas recirculation [1] under a hydrogen pressure of 20-21 atm. with a space velocity of 1.0 hour⁻¹, at a ratio of 12.6 H₂ : HC, and at a temperature of 470-480°. The reactor was loaded with 300 ml of catalyst, which was reduced in a stream of hydrogen at 320-330° for 12 hours. The characteristics of Catalysts 1 and 2, obtained in the reforming of gasoline over Samples 1 and 2 of catalyst are given in Table 4 and in the figure. In the reforming of the fraction only very slight gas formation was observed, and the circulating gas mixture contained up to 99% of hydrogen.



Change in the composition of catalysts obtained over different samples of 0.5% Pd-Al₂O₃ catalyst.

more slowly in Catalystate 2 than in Catalystate 1, which indicates that Sample 2 of 0.5% Pd-Al₂O₃ catalyst was somewhat the more stable. In both catalysts some broadening of fractional composition occurred (74-130.6° and 63-145° after a five-hour run for Catalystates 1 and 2 respectively). Finally, both catalyst samples effected almost complete desulfurization of the fraction (in both catalystates the sulfur content was 0.001%, instead of 0.017% in the original fraction).

TABLE 3

Group Composition of the 89.5-126° Fraction

Class of hydrocarbons	Content (% by weight)
Paraffins including:	52.7
normal	29.3
with tertiary carbon atom	22.5
with quaternary carbon atom	0.9
Cyclopentanes	14.6
Cyclohexanes	18.5
Aromatic hydrocarbons	5.6

TABLE 4

Characteristics of Catalystates obtained in the Reforming of the 89.5-126° Fraction (470-480°; 20 atm; V 1.0 hour⁻¹; 12.6 H₂ : HC)

Time of run over catalyst (hours)	n ²⁰ _D	d ²⁰ ₄	Aromatics content (% by volume)	Time of run over catalyst (hours)	n ²⁰ _D	d ²⁰ ₄	Aromatics content (% by volume)
Catalyzate 1				Catalyzate 2			
5.00	1.4120	0.725	22.0	5.00	1.4175	0.733	29.0
7.50	1.4100	0.723	18.5	14.50	1.4090	0.723	17.0
11.50	1.4085	0.723	16.0	25.00	1.4085	0.723	15.5
16.50	1.4080	0.722	15.0	35.50	1.4075	0.720	14.0
21.50	1.4070	0.720	13.0	45.50	1.4060	0.719	12.0
27.00	1.4065	0.719	12.5				

In the catalystates obtained after the first five hours of work by the catalysts, the individual-hydrocarbon

TABLE 5

Individual Hydrocarbons in Catalyzate 1

Hydrocarbon	Content (% by weight)	Hydrocarbon	Content (% by weight)
Paraffins			
Pentane	1.07	2-Methylhexane	1.10
Hexane	6.89	3-Methylhexane	6.61
2-Methylpentane	1.11	3-Ethylpentane	0.88
3-Methylpentane	1.20	2,2,3-Trimethylbutane	0.09
2,2-Dimethylbutane	0.79	Octane	2.37
2,3-Dimethylbutane	0.26	2,4-Dimethylhexane	2.51
Heptane	19.36	2,3-Dimethylhexane	2.92
2,2-Dimethylpentane	0.35	2-Methylheptane	4.98
2,3-Dimethylpentane	0.98	4-Methylheptane	0.26
2,4-Dimethylpentane	0.45	3-Methylheptane	0.06
3,3-Dimethylpentane	1.10	3-Ethylhexane	0.17
		Total	60.2
Cyclopentane Hydrocarbons			
Methylcyclopentane	0.72	Ethylcyclopentane	1.23
1,1-Dimethylcyclopentane	0.23	1,2,3-Trimethylcyclopentane (cis-trans-cis)	1.04
1,3-Dimethylcyclopentane (trans)	3.65	1,1,3-Trimethylcyclopentane	0.11
1,3-Dimethylcyclopentane (cis)	0.63		
1,2-Dimethylcyclopentane (trans)	3.17	Total	10.8
Cyclohexane Hydrocarbons		Aromatic Hydrocarbons	
Cyclohexane	0.22	Benzene	3.25
Methylcyclohexane	0.51	Toluene	14.75
1,1-Dimethylcyclohexane	0.07	m-Xylene	0.82
1,2-Dimethylcyclohexane	0.07	o-Xylene	0.81
1,4-Dimethylcyclohexane	0.13	p-Xylene	0.35
		Ethylbenzene	0.35
Total	1.0	Total	20.3
		Accounted for (%)	92.3
		Unaccounted for (% of paraffin- -naphthene part of catalyzate)	1.5
		Residue in flask after fractionation (%)	2.5
		Losses (%)	3.7
		Total	100.0

TABLE 6

Individual Hydrocarbons in Catalyzate 2

Hydrocarbon	Content (% by weight)	Hydrocarbon	Content (% by weight)
Paraffins			
Pentane	0.35	Octane	3.42
Hexane	4.25	2,3-Dimethylhexane	0.31
2-Methylpentane	1.11	2,4-Dimethylhexane	2.09
3-Methylpentane	0.95	3,4-Dimethylhexane	0.06
2,2-Dimethylbutane	0.15	2-Methylheptane	0.06
2,3-Dimethylbutane	0.27	3-Methylheptane	0.26
Heptane	17.7	4-Methylheptane	6.18
2,2-Dimethylpentane	0.53	3-Ethylhexane	0.26
2,3-Dimethylpentane	0.94	2-Methyl-3-ethylpentane	0.37
2,4-Dimethylpentane	1.79	2,2,3-Trimethylpentane	0.55
3,3-Dimethylpentane	0.52	2,3,4-Trimethylpentane	0.42
2-Methylhexane	10.63	2,2,5-Trimethylhexane	0.29
3-Methylhexane	8.72		
3-Ethylpentane	0.08		
		Total	62.3
Cyclopentane Hydrocarbons		Cyclohexane Hydrocarbons	
Methylcyclopentane	1.3	Methylcyclohexane	0.61
1,3-Dimethylcyclopentane (trans)	1.44	1,1-Dimethylcyclohexane	0.14
1,2-Dimethylcyclopentane (trans)	1.7		
Total	4.4	Total	0.8
Aromatic Hydrocarbons			
Benzene	1.74	o-Xylene	2.03
Toluene	18.80	p-Xylene	0.87
m-Xylene	2.03	Ethylbenzene	0.87
		Total	26.4
		Accounted for (%)	93.9
		Residue in flask after fractionation (%)	2.3
		Losses (%)	3.8
		Total	100.0

composition was determined by the combined method [20].* The dearomatized part of the catalyzates was fractionated through a column of 75-plate efficiency. The results of the analysis of Catalyzates 1 and 2 are given in Table 5 and 6. The data of Tables 5 and 6 enable us to determine the group compositions of the two catalyzates, which are given in Table 7.

* Raman-spectrum analysis of Catalyzates 1 and 2 was carried out by Iu. P. Egorov, I. P. Iakovlev, and T. M. Ivanova, to whom the authors express their thanks.

It will be seen from a comparison of data on the group compositions of the original fraction and the two catalyzates (see Tables 3 and 7) that contents of cyclohexane hydrocarbons are very much less in the catalyzates (a fall from 18.6% in the original fraction to about 1% in the catalyzates). The fall in the content of cyclopentane hydrocarbons was particularly notable in Catalyzate 2, which contained only 4.4% of cyclopentanes, as compared with 14.6% in the original fraction. On the other hand, the relative amount of paraffins in the catalyzates was appreciably higher (60.2% and 62.3%, respectively, in Catalyzates 1 and 2, as compared with 52.7% in the original fraction). It should be noted that increase in the amount of paraffin hydrocarbons occurred mainly in the component containing tertiary carbon atoms; this was particularly true for Catalyzate 2 (34.6% instead of 22.5% in the original fraction). The increases in the content of aromatics also differed (increases to 20.3% and 26.4% in Catalyzates 1 and 2 from 5.6% in the original fraction).

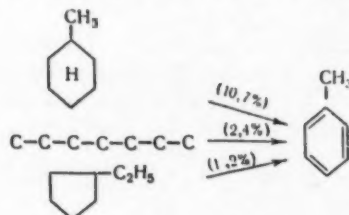
Hence, comparison of group compositions of the original fraction and the catalyzates indicates the occurrence of more profound reforming of the fraction over Sample 2 of 0.5% Pd-Al₂O₃ catalyst, though hydrocarbons of all classes undergo transformations (to differing extents) over both catalyst samples.

TABLE 7
Group Compositions of Catalyzates

Class of hydrocarbons	Content (% by weight) in Catalyzate	
	No. 1	No. 2
Paraffins including:	60.2	62.3
normal	29.7	25.7
with tertiary carbon atom	28.1	34.6
with quaternary carbon atom	2.4	2.0
Cyclopentanes	10.8	4.4
Cyclohexanes	1.0	0.8
Aromatic hydrocarbons	20.3	26.4

In this sense it is particularly of interest to compare the character of individual hydrocarbons found in the original fraction and in Catalyzate 2. It will be seen from a comparison of Table 2 and 6 that only C₅ and C₈ paraffins are present in Catalyzate 2 in almost the same amounts as in the original fraction. Of C₇ hydrocarbons, there are seven present instead of six (0.52% of 2,3-dimethylpentane was found). The content of heptane fell by 2.89%, and that of 2,3-dimethylpentane by 1.36%. At the same time the content of 2,4-dimethylpentane rose by 1.49%, that of 2-methylhexane by 6%, and that of 3-methylhexane by 3.49%. Of C₈ hydrocarbons ten isomers were found instead of four (0.26% of 3-methylheptane, 0.31% of 2,3-dimethylhexane, 0.26% of 3-ethylhexane, 0.37% of 3-ethyl-2-methylpentane, 0.55% of 2,2,3-trimethylpentane, etc.). The content of 2,4-dimethylhexane was increased by 1.34%, and that of 4-methylheptane by 3.15%. At the same time the 2-methylheptane content fell by 3.62%. By the Raman spectrum method it was shown that 2,5- and 3,3-dimethylhexanes were present as well as the ten C₈ isomers given in Table 6. Of the nine cyclopentane hydrocarbons, only three remained in Catalyzate 2; the content of trans-1,2-dimethylcyclopentane fell by 5.44%. Of eight cyclohexane hydrocarbons present in the original fraction, only two were detected in the catalyzate, and these were present in very small amount (0.61% of methylcyclohexane and 0.14% of 1,1-dimethylcyclohexane). The number of aromatic hydrocarbons was increased from four to six. In order of their contents in the fraction the aromatic hydrocarbons fell in the series: toluene, m- and o-xylene, benzene, p-xylene, and ethylbenzene. Hence, as a result of the catalytic treatment of the 89.5-126° fraction over Sample 2 of the 0.5% Pd-Al₂O₃ catalyst (treated with HF) we obtained a catalyzate having a high content of toluene and branched paraffins.

On the basis of this investigation we may represent the formation of the most important hydrocarbon, toluene, by the following scheme:



Other transformations can be inferred by a comparison of the data in Tables 2, 5, and 6.

SUMMARY

1. The reforming of the 89.5-126° fraction of gasoline from Second Baku petroleum was carried out at 470-480° under 20 atm at a space velocity of 1 hour⁻¹ and a reactant ratio of 12.5 H₂ : HC in presence of two different samples of palladium catalyst (0.5% Pd-Al₂O₃) differing with respect to their treatment before use.

2. It was shown that both catalyst samples bring about the dehydrogenation of cyclohexanes, the conversion of cyclopentanes into cyclohexanes with subsequent dehydrogenation, and the desulfurization of the fraction; these processes are accompanied by some broadening of the fractional composition. In presence of Sample 2 of the catalyst, more cyclopentanes and paraffins were drawn into the process of formation of aromatic hydrocarbons than in presence of Sample 1. Also, Catalyzate 2 had a higher content of branched paraffins.

3. The individual-hydrocarbon compositions of the original fraction and the two catalyzates were investigated by the combined method.

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ISOMERIZATION OF SATURATED HYDROCARBONS

COMMUNICATION 1. ISOMERIZATION OF C_6 - C_8 PARAFFINS

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In various papers published in recent years it has been noted that saturated hydrocarbons undergo considerable isomerization under pressure, in presence of hydrogen and a catalyst, generally an aluminosilicate or halogenated alumina containing an addition of a Group VIII metal [1-4]. It must be mentioned that such heterogeneous isomerization of saturated hydrocarbons has already found extensive industrial application in all sorts of modifications of the catalytic reforming of low-octane straight-run gasolines (platforming, houdryforming, catforming, etc.).

Whereas adequate attention has been devoted to questions relating to the preparation of so-called bifunctional catalysts and to the conditions under which the processes are carried out, much less work has been done on the reactions of individual hydrocarbons under the same conditions. In most cases only the reactions of n-alkanes have been investigated. An exception is found in the work of Clapetta and Hunter [4], in which the isomerization of some C_6 and C_7 isoparaffins was investigated. As the investigation of the isomerization of individual hydrocarbons of various structures is of undoubted interest, both for the elucidation of the mechanism of isomerization reactions and for the study of the thermodynamic and kinetic parameters of the reactivity of hydrocarbons, it was decided to make a systematic study of the isomerizations of a large number of individual hydrocarbons.

EXPERIMENTAL

The isomerizations of hydrocarbons were investigated in a flow system in an apparatus designed specially for the study of reactions occurring under pressure. The basic arrangement of the apparatus was described in papers by Shulkin and co-workers [3]. The apparatus that we used also included a pressure control, which enabled us to maintain a given pressure regardless of the amount of hydrogen passing through the apparatus [5]. We used a Houdry-type aluminosilicate catalyst carrying 0.5% of platinum by weight (applied by impregnation with chloroplatinate solution). The initial activity of the catalyst was checked for the isomerization of n-heptane. At 370° and 10 atm with a space velocity of 1.0 hour⁻¹ and a molar ratio of hydrogen to original hydrocarbon of 4, the yield of C_7 isoparaffins was 70% for a total yield of liquid products of 90-92%. We must point out that, in this case, increase in pressure led to the intensification of hydrocracking reactions and lowering of the yield of liquid products (to 80% at 25 atm).

All experiments on the isomerization of individual hydrocarbons were carried out at 10 atm with a molar ratio of hydrogen to original hydrocarbon of 4 and a space velocity of 1.0 hour⁻¹. The temperatures of the experiments were 380° for C_6 paraffins, 370° for C_7 paraffins, and 360° for C_8 paraffins. The results of work on isomerization naturally depend largely on the accuracy of the analysis of hydrocarbon mixtures in the catalyzates. For this purpose American investigators have used the mass spectrograph, in which case concentrations of separate components may be measured accurately within 1%. We have used Raman and infrared spectrum analysis.

Raman spectra were recorded photographically on an ISP-51 spectrograph; the blue and violet mercury lines 4358 and 4047 Å were used as exciting radiation. The frequencies (wave numbers) of the lines were determined by the comparison of negatives on an IZA-2 comparator and determination of the values from a graph for the dispersion of the apparatus. The intensities of the lines were estimated visually in the course of the comparison and were corrected in a subsequent examination of the spectrum with a DSP-1 spectrum-projector. The frequencies

and intensities of the lines were mean values obtained from three and two spectra respectively. For details of the procedure see the literature [6, 7]. In order to determine the intensities of individual Raman lines with greater accuracy, we determined the spectra, under the same conditions, of the individual paraffins having the highest concentrations in the mixtures investigated (2-methylpentane, 3-methylhexane, 3-methylheptane). In some cases we also made measurements on artificial mixtures of paraffins at concentrations close to those in the isomerizates obtained in our experiments.

TABLE 1

Properties of Hydrocarbons Used In This Work.

Hydrocarbon	B.p. (°C)	n_D^{20}	d_4^{20}	Method of preparation
3-Methylpentane	62.5-63	1.3765	0.6641	From ethylmagnesium bromide and 2-butanone via 1-ethyl-1-methyl-1-propanol
2-Methylhexane	90-91	1.3849	0.6786	From butylmagnesium bromide and acetone via 1,1-dimethyl-1-pentanol
3-Methylhexane	91.5-91.6	1.3884	0.6860	From propylmagnesium bromide and 2-butanone via 1-ethyl-1-methyl-1-butanol
2,3-Dimethylpentane	89-90	1.3917	0.6950	From isopropylmagnesium bromide and 2-butanone via 1-ethyl-1,2-dimethyl-1-propanol
2,2-Dimethylpentane	79-80	1.3828	0.6750	From tert-butylmagnesium chloride and allyl bromide
3-Ethylpentane	93-93.5	1.3935	0.6969	From ethylmagnesium bromide and ethyl propionate via 1,1-diethyl-1-propanol
Octane	125-125.5	1.3974	0.7027	Dehydration of octyl alcohol
2-Methylheptane	117-118	1.3953	0.6975	From methylmagnesium iodide and 2-heptanone via 1,1-dimethyl-1-hexanol
2,4-Dimethylhexane	108-108.5	1.3956	0.7009	From ethylmagnesium bromide and 4-methyl-2-pentanone via 1,3-dimethyl-1-ethyl-1-butanol
2,2,3,3-Tetramethylbutane	105-106	m.p. 100°		From methylmagnesium bromide and 2-chloro-2,3,3-trimethylbutane

Infrared spectroscopy enabled us to obtain a more accurate picture of the average degree of branching in the sample under investigation, the results being applied mainly in the quantitative determination of the n-alkanes. The degree of branching was determined from ratios of optical densities of absorption bands in the region

$$3.51 - 3.38 \mu \quad \frac{13.51}{13.38} ; \quad \frac{13.42}{13.38} .$$

Details of this method have already been published [8, 9]. In this work we measured the corresponding ratios for C_6-C_8 normal, monomethyl-, and dimethyl-substituted paraffins and also for mixtures of isomers differing in degree of branching. For the correct interpretation of the infrared spectra of the isomerizates it was necessary to separate normal from dimethyl-substituted hydrocarbons, which was carried out by fractionation through a column of 15-plate efficiency. The catalyzates were also fractionated through a 35-plate column, by which means it was possible to separate n-alkanes and also mixtures of 2- and 3-methylalkanes, of which the isomerizates largely consisted. From the properties of this isolated fraction we were able to determine the relative amounts of 2- and 3-methylalkanes and so check the results of spectrum analyses.

The hydrocarbons used in the work were synthesized by Grignard and Grignard-Wurtz reactions. The tertiary alcohols isolated as intermediate products were dehydrated over pure alumina at 280°. The olefins were hydrogenated over platinized charcoal at 180-200°. The methods of preparing the paraffins, and their properties, are given in Table 1.

Results on the isomerization of ten individual paraffins, and also the results of Ciapetta and Hunter [4] (marked

with an asterisk), are given in Tables 2-4. These tables give also equilibrium concentrations, calculated from the data of Rossini and co-workers [10], for these paraffins at temperatures corresponding to our experimental conditions. It will be seen from Tables 2-4 that the isomerization of normal and slightly branched paraffins proceeds fairly rapidly, and, in general, the concentrations of the separate components in the isomerizates are in accord with Rossini's calculations. However, the conversion of slightly branched paraffins into hydrocarbons having several branchings, and also into hydrocarbons containing quaternary carbon atoms, proceeds much less readily, so that in the isomerization of normal and slightly branched paraffins a special sort of "equilibrium" is set up which we shall call "realizable equilibrium".* A characteristic feature of this "realizable equilibrium" is that, in absolute magnitude, the concentrations of normal and monosubstituted alkanes are higher than the calculated values because of the absence, or presence in insignificant amount, of highly branched paraffins. However, the relative amounts of normal and monosubstituted alkanes are in full accord with Rossini's calculations. In Tables 2-4 "realizable-equilibrium" concentrations are given, these being concentrations of C_6 - C_8 paraffins, which, according to calculation, would be formed if the isomerization is largely displaced in the direction of normal and monosubstituted hydrocarbons (for C_8 paraffins, 2,4- and 2,5-dimethylhexanes are included also). In practice the "realizable equilibrium" composition is calculated as follows.

In those cases in which it was possible (C_6 and C_7 paraffins), account was taken of the actual amount of disubstituted hydrocarbons formed (e.g., the total content of 2,3- and 2,2-dimethylbutanes formed in the isomerizations of hexane, 2-methylpentane, and 3-methylpentane was 10%). The remainder (90% in the case cited) was distributed between hexane and 2- and 3-methylpentanes; the relative amounts of the isomers were determined from equilibrium constants calculated from Rossini's data. For hydrocarbons of higher molecular weight (C_8), in view of the impossibility of estimating quantitatively the highly branched hydrocarbons formed, the calculation of realizable equilibrium was carried out on the basis of only the equilibrium constants of the six C_8 paraffins actually formed. It will readily be observed that the agreement between calculated "realizable equilibrium" concentrations and the experimental values is fairly good for the isomerization of normal, monosubstituted, and some disubstituted alkanes. We may add that under the given conditions the production of an ideal equilibrium mixture is practically impossible, because increase in time of contact, raising the temperature, or increasing the activity of the catalyst results not only in increase in degree of isomerization, but also in intensification of hydrocracking reactions, to which branched hydrocarbons are usually the most prone (see data on selectivity factor in Tables 2-4).

It must be pointed out that some error must have crept into the values given by Rossini for the free energy of 2,3-dimethylpentane; it is probable that the actual value is considerably higher. This is evident from the fact that the isomerizate from 2,3-dimethylpentane contained not more than 5% of the original paraffin, whereas according to Rossini's data there should be 25% of the original paraffin. This far-reaching isomerization of 2,3-dimethylpentane was established by comparison between the Raman spectrum of the isomerizate with that of a specially prepared mixture of heptane, 2-methylhexane, 3-methylhexane, and 2,3-dimethylpentane (25%). Also, distillation of the 2,3-dimethylpentane isomerizate through a column yielded a fraction of b.p. 88-92° (b.p. of 2,3-dimethylpentane 89.8°) which, according to infrared spectrum data, consisted almost entirely of monosubstituted C_7 hydrocarbons. It is interesting that theoretical calculations of the heat of formation and free energy of 2,3-dimethylpentane carried out by Tatevskii were also greater than the values cited by Rossini, the discrepancies being 1000 cal/mole for ΔH_{25}^0 and 2850 cal/mole for ΔZ_{327}^0 [11]. Judging from our experimental results, the free energies given by Rossini and co-workers for paraffins other than 2,3-dimethylpentane are extremely accurate. The discrepancies between calculated concentrations of paraffins in equilibrium mixtures and the values observed in our experiments did not exceed the errors of experiment and analysis.

Although we did not carry out any special investigations on the kinetics of the isomerization of individual

* Strictly speaking, this cannot be called an equilibrium state, because when we proceed from the side of highly branched paraffins we do not obtain isomerizates of the same composition. It is therefore more correct to speak of actually attainable concentrations, which is understood to mean concentrations that can be obtained in the isomerization of normal and slightly branched paraffins under the given conditions over the given catalyst. However, calculated values of concentrations of components corresponding to realizable equilibrium provide an adequate general picture of the isomerization processes and are of great practical importance, particularly in the estimation of the possibilities of isomerization in hydrocarbons of comparatively high molecular weight.

hydrocarbons, we can make some rough comparisons. Thus, the rates of isomerization of C_6 paraffins rise in the following order: 2,2-dimethylbutane, 2,3-dimethylbutane < hexane < 2-methylpentane < 3-methylpentane. It is interesting that the corresponding series for C_6 olefins (in presence of a pure aluminosilicate catalyst) forms a rather different sequence: 2,3-dimethyl-2-butene < 2-methyl-2-pentene < 3-methyl-2-pentene < hexene < 3,3-dimethyl-1-butene [12]. The rates of isomerization of C_7 paraffins rise in the following order: 2,2,3-trimethylbutane < heptane < 2,4-dimethylpentane < 2,2-dimethylpentane < 2,3-dimethylpentane < methylhexanes < ethylpentane.

TABLE 2

Isomerizations of C_6 Paraffins

Original hydrocarbon	Temperature of experiment (°C)	Composition of isomerizate (%)					Ratio 2-methylpentane : 3-methylpentane	Combined 1- and 3-methylpentanes (%)	Selectivity factor (concentration of C_6 fraction in catalyze)
		Hexane	2-Methylpentane	3-Methylpentane	2,3-Dimethylbutane	2,2-Dimethylbutane			
Hexane*	385	25	38	25	6	6	1.5	63	0.91
2-Methylpentane*	385	25	37	26	7	6	1.4	63	0.94
3-Methylpentane	380	15-20	45-50	25	Traces	~5	2	65-70	—
2,3-Dimethylbutane*	371	16	24	15	33	12	1.6	39	0.97
2,2-Dimethylbutane*	372	8	10	6	11	65	1.7	16	0.98
Equilibrium mixture at 377° according to Rossini's results**	—	21	32	18	10	19	1.8	50	—
Realizable equilibrium at 377°	—	27	39	22	Combined 2,2 + 2,3 = 10%		1.8	61	—

* According to data of [4].

** Change in temperature of the order of several tens of degrees has little effect on the composition of the equilibrium mixture. Hence, the calculated compositions of equilibrium mixtures are given here and below only for one temperature, corresponding approximately to the mean temperature used in the experiments.

Mechanism of the Isomerization of Paraffins

Before proceeding to direct considerations of the mechanism of isomerization, i.e., to the elucidation of the ways in which the hydrocarbons pass from one structural form to another, we must consider some general questions concerning the chemistry of the processes occurring in presence of hydrogen over multifunctional catalysts. Any catalyst used for the isomerization of saturated hydrocarbons has at least two active functions: a) isomerization, which is usually effected by an aluminosilicate or by alumina activated by treatment with hydrofluoric acid; b) hydrogenation-dehydrogenation, which is usually effected by additions of Group VIII metals, most frequently platinum or nickel.

Let us first examine some questions relating to the character of the interaction between the isomerization and hydrogenation functions of the catalyst and also to the part played by hydrogen and pressure in the catalytic process. It must be stated that some of these questions have already been discussed in previous papers [13]. It is quite natural, therefore, that we shall need to make use both of part of these published experimental data and also of the conclusions arrived at in these previous publications. We shall supplement these facts by new data which we ourselves have obtained and try to give a general picture of the isomerization of saturated hydrocarbons in presence of multifunctional catalysts. There can be no doubt that the presence of Group VIII metals as catalyst

TABLE 3

Isomerizations of C₇ Paraffins

Original hydrocarbon	Temperature of experiment, °C	Composition of isomerizate (%)								Combined 2- and 3-methylheptanes (%)	Ratio 2-methyl-3-methylheptane	Selectivity factor
		heptane	2-methylhexane	3-methylhexane	2,3-dimethylpentane	2,4-dimethylpentane	2,2-dimethylpentane	3,3-dimethylpentane	2,2,3-trimethylbutane			
Heptane	353	22	27	45	—	6	—	—	—	72	0,6	0,86
2-Methylhexane	370	15-20	20-25	45	Traces?	5	5	Traces	—	65-70	0,45-0,5	0,85
3-Methylhexane	370	15-20	20-25	45	Traces?	5	5	—	—	65-70	0,45-0,5	0,85
2,3-Dimethylpentane	370	Traces	30	45	5	15	—	—	—	75	0,6	0,75
2,4-Dimethylpentane*	313	2	12	43	24	27	14	8	—	23	0,9	0,94
Ditto*	343	7	16	15	9	7	5,5	4,5	—	31	1,05	0,65
2,2-Dimethylpentane	370	10	25	45	Traces	5-10	10	—	1	70	0,55	0,75
2,2,3-Trimethylbutane*	354	—	6	12	5	5	6	—	66	18	0,5	0,93
3-Ethylpentane	370	20	25	45	—	5	5	—	Traces	70	0,55	0,85
Equilibrium mixture at 377° acc. to Rossini's results	—	11,5	16,5	22,5	25	6	6	7	3	39	0,73	—
Realizable equilibrium at 377°	—	21	28	41	—	Combined 2,2 + 2,4 = 10%		—	—	69	0,73	—

TABLE 4

Isomerizations of C₈ Paraffins

Original hydrocarbon	Temperature of exp. (°C)	Composition of isomerizate (%)						Remain- ing 12 C ₈ paraf. comb. (%)	Total mono- substi- tuteds (%)	2-methyl- heptane; 3-methyl- heptane	Selecti- vity factor
		Composition of isomerizate (%)									
		octane	2-methyl- heptane	3-methyl- heptane	4-me- thyl- heptane	2,4-dimethyl- hexane	2,5-dimethyl- hexane				
Octane*	316	38	41	33	18	—	—	—	62	0.3	0.97
Ditto*	348	21	24	26	14	—	—	—	64	0.9	0.68
" "	360	30	60% of monosubstituteds			10% of disubstituteds; 2,4- dimethylhexane detected		—	60	—	0.85
2-Methylheptane	360	10	70% of monosubstituteds; 2- and 3-methylheptanes detected			20% of disubstituted, mainly 2,4- with some 2,5-di- methylhexane detected		—	70	—	0.8
2,4-Dimethylhexane	360	—	50% of monosubstituteds; 2- and 3-methylheptanes detected			35—40		—	50	—	0.65
2,2,3,3-Tetramethyl- butane	360										
equilibrium mixt. at 377°	360			18	6	Does not isomerize		—	—	—	~1.0
acc. to Rossini's results	—	10	16		11		9	30	40	0.89	—
Realizable equilibrium*											
(taking account of 6 isomers)	—	14	23	26	9	16	12	—	58	0.89	—

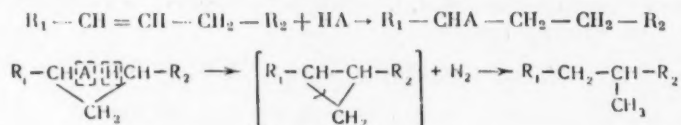
components results in the dehydrogenation of alkanes to alkenes and of cycloalkanes to cycloalkenes and further to aromatic hydrocarbons. As a separate paper will be devoted to the transformations of cycloalkanes, we shall examine here only the reactions of alkanes. According to calculations from data in the literature [14], at 377° the equilibrium mixture of hexane \rightleftharpoons hexene + H₂ contains 10% of alkenes [14]. In our experiments on the passage of heptane over a multifunctional catalyst in a stream of hydrogen at 377° and atmospheric pressure, a catalyzate containing about 12% of unsaturated hydrocarbons was obtained, which is in close accord with the calculations of Frost [14].

Increase in the pressure of the hydrogen lowers the equilibrium concentration of olefins to 1% at 25 atm and 3% at 10 atm (hexane 377°). In our isomerization experiments, however, the actual concentration of olefins was still less owing to the use of a threefold excess of hydrogen. At such a low concentration of olefins (a few tenths of a percent) polymerization and hydrogen-redistribution processes no longer occur, i.e., the complex group of transformations of olefins generally associated with catalytic cracking, which is one of the main sources of the deposition of carbonaceous material on aluminosilicate catalysts, does not occur. It is for this reason that the catalyst surface remains clean for a long time, a fact which contributes to the preservation of the activity of the catalyst. On the other hand, as already stated, even under high pressures, paraffins in contact with a multifunctional catalyst give rise to a certain amount of olefins, which will probably undergo isomeric changes just as they do in presence of acidic catalysts. However, by the use of a sufficiently high pressure we may evidently suppress the formation of olefins to such an extent that isomerization will be retarded. In the investigation [4], in fact, it was found that increase in pressure in the isomerization of hexane reduced the yield of branched hydrocarbons to an appreciable extent, but at atmospheric pressure isomerization did not go and severe hydrocracking was observed. Thus, increase in pressure for 10 to 20 atm halves the yield of branched C₆ hydrocarbons, while at 50 atm reaction stops altogether. However, with rise in temperature the effect of pressure on the isomerization is gradually reduced, and at 410° it almost disappears (checked up to 50 atm). There can be no doubt, however, that by the use of still higher pressures appreciable retardation of the isomerization can be produced even at this temperature.

In our opinion, another role of hydrogen, and also of pressure, consists in increasing the rates of hydrogenation-dehydrogenation reactions, so that almost every molecule of the original paraffin could be subjected to these changes. It will be understood that the rate-determining reaction here is hydrogenation (a bimolecular reaction proceeding at a low concentration of olefins), whereas direct isomerization, i.e., change in the carbon skeleton of the hydrocarbon, proceeds fairly quickly because of its ionic character. The term "rate of the hydrogenation-dehydrogenation reaction" has here a somewhat unusual meaning, because the apparent rate of reaction is zero; except, of course, in the initial moments, no change in the concentration of olefins occurs. However, because of the known dynamic character of equilibrium, new paraffin molecules are constantly being brought into reaction. There are indications (admittedly for quite a different reaction) that the rate of reaction, or more accurately the relative number of molecules reacting in unit time, at the point of equilibrium differs little from the rate of the same reaction at a point far removed from equilibrium [15]. All this gives reason to maintain that alkenes (or, as the Americans call them, "potential alkenes") are direct participants in the isomerization of alkanes.

Apart from these considerations, there is various indirect experimental evidence indicating that alkenes take part in the isomerization of saturated hydrocarbons. This includes the complete loss of the activity of the catalyst after treatment with organic bases (pyridine and other amines). Similar loss in catalytic activity with respect to the isomerization of olefins is known also for aluminosilicate catalyst and for activated alumina. Treatment with sodium carbonate, i.e., cation exchange with replacement of hydrogen by sodium, also results in the poisoning of the multifunctional catalyst. We must point out that treatment of the multifunctional catalyst with pyridine or sodium carbonate results in the poisoning only of the isomerization function (the acidic part) of the catalyst, which, while becoming inactive with respect to isomerization, preserves its activity with respect to dehydrogenation, e.g., that of cyclohexane into benzene. On the other hand, examples may be cited in which the hydrogenation-dehydrogenation function of the catalyst is poisoned and its isomerization activity is preserved (completely only with respect to olefins, of course). Poisoning with sulfur compounds is a case in point [16]. Another proof of the direct participation of olefins in the reactions is the considerable hydrocracking of certain highly branched paraffins. We showed previously that, in presence of an aluminosilicate catalyst, olefins having substituents in β -positions to one another undergo much more decomposition than olefins of other structures [17]. Diisobutylene decomposes particularly readily in presence of an aluminosilicate. An analogous relationship also exists between the structures of paraffins and their tendencies to undergo hydrocracking in presence of a multifunctional catalyst. Thus, at 360° and 10 atm, 2,2,4-trimethylpentane is almost completely converted into isobutane, though it remains unchanged in presence of pure

aluminosilicate or platinized aluminosilicate poisoned with pyridine. Moreover, it can be seen from the data in Tables 2-4 that the lowest selectivity factors among the C_7 and C_8 paraffins are possessed by 2,4-dimethylpentane and 2,4-dimethylhexane, which can be associated closely with the considerable hydrocracking of these hydrocarbons. Finally, study of the hydrocracking products from paraffins showed that, under these conditions, the hydrocarbon molecule is broken preferentially in the middle of the chain, which is very characteristic also for the catalytic cracking of olefins over an aluminosilicate catalyst. Hence, the species undergoing direct isomerization is an olefin, whose change in structure is to be explained by the presence of mobile hydrogen ions on the catalyst surface. The isomerization process can be represented as follows: the olefin formed is chemisorbed on the catalyst surface, and a hydrocarbon molecule is regenerated with removal of a portion from the carbon atom in the β -position with respect to the carbon attached to the catalyst. The resulting alkylcyclopropane is hydrogenated with formation of an isomer of the original paraffin.



The intermediate alkylcyclopropane form is enclosed in brackets because the closing of the new carbon-carbon bond and the hydrogenation of the old one probably proceed almost simultaneously and the life of the cyclic form is very short.

The above mechanism of the isomerization of paraffins is very close to that proposed by one of us for the direct isomerization of olefins [12]. However, the course of the isomerization of saturated hydrocarbons must be affected to a certain extent by the laws governing the hydrogenation of alkylcyclopropanes, namely, addition of hydrogen to the most highly hydrogenated carbon atom. It is to this circumstance that we can attribute the comparatively high stabilities of the 2,2-dimethyl- and 2,2,3-trimethyl-butane structures. Particular attention should be paid to the stability of the 2,2,3,3-tetramethylbutane structure: this compound does not undergo isomeric change under the given conditions in spite of the fact that, on thermodynamic considerations, this compound should be highly reactive. It is clear that the stability of this paraffin, which incidentally does not undergo degradation either (under the given conditions), can be explained only by the impossibility of its conversion into olefins, which again provides evidence of the direct participation of unsaturated hydrocarbons in isomerization and hydrocracking reactions.

In conclusion we must point out that in isomerization at lower temperatures some departures are observed from the thermodynamic compositions of the catalyzates. Thus, in the isomerization of n-octane at 316° the yields of 3- and 4-methylheptanes are relatively high and that of 2-methylheptane is low. The explanation of this fact must be sought in the primary isomerization act, i.e., in the formation of olefins. The double bond of the octenes formed is probably predominantly near to the center of the chain, which leads to the preferential formation of monomethylated C_8 paraffins with the methyl group positioned centrally. In experiments at higher temperatures, however, an approach to thermodynamic equilibrium between the individual components is established (see Table 4, experiments with n-octane at 348° and 360°).

SUMMARY

1. A systematic experimental investigation was carried out on the isomerization of C_6 - C_8 paraffins under a pressure of hydrogen, and the experimental data obtained are compared with thermodynamic calculations.
2. A mechanism is proposed for the isomerization of saturated hydrocarbons in presence of multifunctional catalysts, and in this mechanism the first stage of the reaction is the formation of olefins.
3. Some new data were obtained on the relation between structure and reactivity in hydrocarbons.

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**In Russian.

HETEROCYCLIC COMPOUNDS

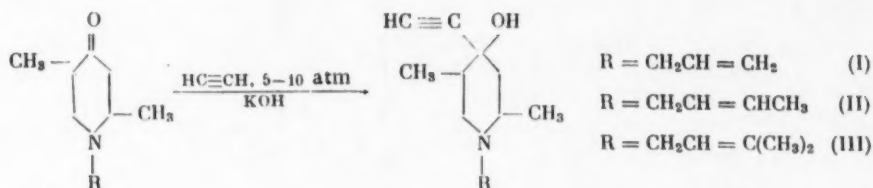
COMMUNICATION 58. SYNTHETIC ANESTHETICS

XIX. SYNTHESIS OF BENZOIC AND PHENOXYACETIC ESTERS OF 1-ALKENYL-4-ETHYNYL-2,5-DIMETHYL-4-PIPERIDINOLS

I. N. Nazarov and A. Sh. Sharifkanov

A systematic investigation is being carried out in our laboratory on the synthesis of new anesthetics from various 4-piperidones [1-4]. The object of the present work was the determination of the effect of unsaturated groups attached to the nitrogen on the physiological (anesthetic) activity of benzoic and phenoxyacetic esters of 4-ethynyl-2,5-dimethyl-4-piperidinols.

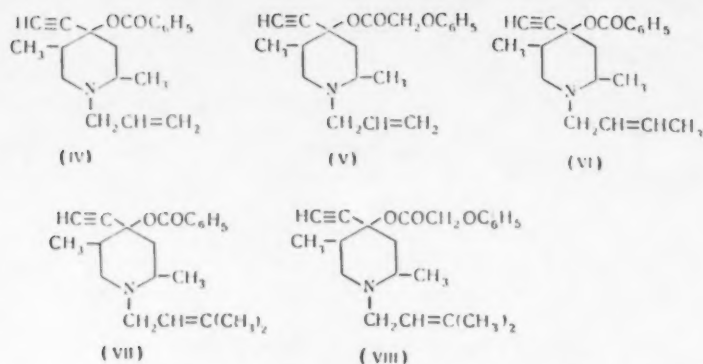
The original 1-alkenyl-4-ethynyl-2,5-dimethyl-4-piperidinols (I)-(III) were synthesized in high yield (above 70%) by the condensation of acetylene under pressure [5] with 1-alkenyl-2,5-dimethyl-4-piperidones, which were described in a previous communication [6].



By this reaction the 1-alkenyl-4-ethynyl-2,5-dimethyl-4-piperidinols (I)-(III) are obtained as liquid mixtures of stereoisomers which are difficult to separate.

In order to isolate the individual compounds the liquid mixture of isomers was converted into crystalline hydrochlorides, which were fractionally crystallized from alcohol; the individual hydrochlorides so obtained were reconverted into the free bases. In this way, from the mixture of isomeric 1-allyl-4-ethynyl-1,5-dimethyl-4-piperidinols (I) we isolated two individual isomers; the α -form of m.p. 92-93° (17% of the total amount of mixture) and the β -form of m.p. 78-79° (3% of the total amount of mixture). From the mixture of isomeric 1-(2-butenyl)-4-ethynyl-2,5-dimethyl-4-piperidinols (II) we isolated only the γ -isomer of m.p. 79-80° (17%), and the residue was difficult to separate by fractional crystallization. From the mixture of isomeric 4-ethynyl-2,5-dimethyl-1-(3-methyl-2-butenyl)-4-piperidinols (III) we isolated two isomers; the γ -form of m.p. 90-91° (25%) and the β -form of m.p. 85-86° (5%). After the isolation of the amounts of individual isomers indicated above, the residual amount of piperidinols remained as an unresolved mixture of isomers.

For the purposes of pharmacological investigation we synthesized the benzoic and phenoxyacetic esters of 1-alkenyl-4-ethynyl-2,5-dimethyl-4-piperidinols (IV)-(VIII), which were obtained by the esterification of the piperidinols (I)-(III) by benzoyl and phenoxyacetyl chlorides in dry pyridine or benzene solution [7].



The esters (IV)-(VIII) so obtained were tested in the form of their hydrochlorides for surface anesthesia by Renier's method in M. D. Mashkovskii's laboratory (Ordzhonikidze VNIKhFI).^{*} The anesthetic effects of these esters were estimated by comparison with those of procaine and tetracaine. The γ -isomers of the phenoxyacetic esters (V) and (VIII) have very feeble anesthetic effects. The benzoic ester of the γ -form of 4-ethynyl-2,5-dimethyl-1-(3-methyl-2-butenyl)-4-piperidinol (VII) was sparingly soluble in water and was not tested, and the β -form of (VII) was found to be an irritant. Only the benzoic esters (IV) and (VI) are highly active, and the benzoic ester of the γ -form of 1-(2-butenyl)-4-ethynyl-2,5-dimethyl-4-piperidinol (VI) was found to be particularly interesting: the anesthetic activity of a 1% solution is equal to that of tetracaine at the same concentration, and its toxicity is less than that of tetracaine by a factor of nearly 3.5. The results of the tests on these two esters are given in the table. As will be seen from the table, the ester (IV) suffers a great loss of activity during sterilization (in 0.25%

TABLE

Substance tested	M.p. of hydrochloride (°C)	Anesthesia index			Index after sterilization at concentration of 0.25%	Mean lethal dose (mg/ kg)
		concentration(%)				
		0.25	1	2		
Procaine				479		63.1
Tetracaine		1300	1300			8.5
Ester (IV)	175-176 (γ-form)	923	1300		381	
Ester (VI)	211-212 (γ-form)	629	1300		773	29.2

solution), whereas the benzoic ester of 1-(2-butenyl)-4-ethynyl-2,5-dimethyl-piperidinol (VI) is quite stable to sterilization.

EXPERIMENTAL

1-Allyl-4-ethynyl-2,5-dimethyl-4-piperidinol (I). The condensation of 4-piperidones with acetylene under pressure was carried out in the 1.5-liter metal reactor described in a previous communication [5]. The reactor was charged with 400 ml of dry ether and 105 g of potassium hydroxide powder. Air was displaced from the reactor with nitrogen and with vigorous stirring and cooling to -8° the mixture was saturated with acetylene at 6 atm, this pressure being maintained throughout the reaction. A solution of 157 g of 1-allyl-2,5-dimethyl-4-piperidone (b.p. 76° (2 mm); n_D^{20} 1.4750) [6] in 200 ml of dry ether was then passed into the reactor over a period of two hours through a metal dropping funnel working under pressure. After the addition of the piperidone the mixture was stirred further for 30 minutes and was hydrolyzed with water (210 ml). The ethereal layer was separated, the aqueous layer was extracted with ether, and the product was neutralized with carbon dioxide and dried with calcined sodium sulfate. Ether was distilled off, and vacuum fractionation of the product gave 143.5 g (80%) of a mixture of stereoisomeric 1-allyl-4-ethynyl-2,5-dimethyl-4-piperidinols (I) as a thick liquid; b.p. $92-94^{\circ}$ (2 mm); n_D^{20} 1.5000; d_4^{20} 0.9836; found MR 57.80; calculated MR 58.35.

^{*} Transliteration of Russian - Publisher's note.

Found %: N 7.17; 7.11. $C_{12}H_{19}ON$. Calculated %: N 7.28.

The mixture of stereoisomeric piperidinols did not crystallize when cooled, and they were converted into their hydrochlorides. By fractional crystallization from absolute alcohol we obtained two individual hydrochlorides:

1) The hydrochloride of the γ -isomer of m.p. 212-213°, amounting to 47 g (29% of the original mixture of isomers).

Found %: Cl 15.33; 15.47. $C_{12}H_{20}ONCl$. Calculated %: Cl 15.45.

The hydrochloride was treated with sodium carbonate solution, and the base was extracted with ether. On removal of ether the residue solidified. The product was recrystallized from petroleum ether; the γ -isomer of the piperidol (I) had m.p. 92-93°.

Found %: N 7.22; 6.99. $C_{12}H_{19}ON$. Calculated %: N 7.28.

2) The hydrochloride of the β -isomer of m.p. 193-194°, amounting to 5 g (3% of the original mixture of isomers).

Found %: Cl 15.61; 15.80. $C_{12}H_{20}ONCl$. Calculated %: Cl 15.45.

The hydrochloride was converted into the free base, i.e., the β -form of the piperidinol (I), m.p. 78-79°.

Found %: N 7.36; 7.12. $C_{12}H_{19}ON$. Calculated %: N 7.28.

A mixture of the γ -form (m.p. 92-93°) and β -form (m.p. 78-79°) melted at 58-63°, and a mixture of their hydrochlorides at 165-175°.

1-(2-Butenyl)-4-ethynyl-2,5-dimethyl-4-piperidinol (II). In the reaction we took 450 ml of dry ether, 70 g of potassium hydroxide powder, and 118 g of 1-(2-butenyl)-2,5-dimethyl-4-piperidone [b.p. 87-89° (2 mm); n_D^{20} 1.4761] [6]. The procedure was as described above. The product, amounting to 100 g (76%), was a mixture of stereoisomeric 1-(2-butenyl)-4-ethynyl-2,5-dimethyl-4-piperidinols (II), obtained in the form of a thick non-crystallizing liquid; b.p. 98-102° (2 mm); n_D^{20} 1.5020; d_4^{20} 0.9781; found MR 62.54; calculated MR 62.94.

Found %: N 7.01; 6.80. $C_{13}H_{21}ON$. Calculated %: N 6.75.

By fractional crystallization of the hydrochlorides from absolute alcohol we isolated 20 g (17% of the total mixture) of an individual hydrochloride, m.p. 208-209°.

Found %: Cl 14.65; 14.58. $C_{14}H_{22}ONCl$. Calculated %: Cl 14.55.

The hydrochloride was treated with sodium carbonate solution, and the base liberated was extracted with ether. The product was the γ -form of the piperidinol (II), m.p. 79-80°.

Found %: N 6.79; 7.09. $C_{13}H_{21}ON$. Calculated %: N 6.75.

4-Ethynyl-2,5-dimethyl-1-(3-methyl-2-butenyl)-4-piperidinol (III). In the reaction we took 98 g of potassium hydroxide powder, 500 ml of dry ether, and 162 g of 2,5-dimethyl-1-(3-methyl-2-butenyl)-4-piperidone [b.p. 84-86° (1 mm); n_D^{20} 1.4810] [6]. Vacuum fractionation of the product gave 130 g (73%) of a mixture of stereoisomeric 4-ethynyl-2,5-dimethyl-1-(3-methyl-2-butenyl)-4-piperidinols (III) in the form of a thick, noncrystallizing liquid; b.p. 118-120° (2 mm); n_D^{20} 1.5030; d_4^{20} 0.9692; found MR 67.44; calculated MR 67.58.

Found %: N 6.44; 6.35. $C_{14}H_{23}ON$. Calculated %: N 6.33.

By fractional crystallization of the hydrochlorides from absolute alcohol we isolated 36 g (25% of the total mixture) of the hydrochloride of the γ -isomer, m.p. 205-206°.

Found %: Cl 13.50; 13.24. $C_{14}H_{24}ONCl$. Calculated %: Cl 13.77.

The hydrochloride was converted into the free base, i.e., the γ -form of the piperidinol (III), m.p. 90-91° (from petroleum ether).

Found %: N 6.43; 6.22. $C_{14}H_{23}ON$. Calculated %: N 6.33.

The mixture of hydrochlorides remaining after the isolation of the γ -isomer was converted into the free base, and this crystallized partially after prolonged standing. The crystals were pressed off at the water pump and

recrystallized from petroleum ether; we then obtained 6.2 g (about 5% of the total mixture) of the β -isomer of the piperidinol (III), m.p. 85-86°.

Found %: N 6.55; 6.50. $C_{14}H_{23}ON$. Calculated %: N 6.33.

The hydrochloride of the β -isomer melts at 147-148°.

Found %: Cl 14.05. $C_{14}H_{24}ONCl$. Calculated %: Cl 13.77.

A mixture of the γ -form (m.p. 90-91°) and the β -form (m.p. 85-86°) melted at 58-62°, and a mixture of their hydrochlorides at 143-168°.

Benzoic Ester of the γ -Form of 1-Allyl-4-ethynyl-2,5-dimethyl-4-piperidinol (IV). A mixture of 4.6 g of the hydrochloride of the γ -form of 1-allyl-4-ethynyl-2,5-dimethyl-4-piperidinol (m.p. 212-213°), 8.4 g of benzoyl chloride, and 10 g of dry pyridine was heated at 120-125° for two hours and left overnight. On the next day the product was diluted with 30 ml of dry ether; the precipitate was filtered off and recrystallized twice from absolute alcohol. The product (3.4 g) was the hydrochloride of the benzoic ester of the γ -form of 1-allyl-4-ethynyl-2,5-dimethyl-4-piperidinol, m.p. 175-176°.

Found %: C 68.40; 68.45; H 7.47; 7.36; N 4.43; 4.50; Cl 10.62; 10.66. $C_{19}H_{24}O_2NCl$. Calculated %: C 68.30; H 7.24; N 4.19; Cl 10.63.

Phenoxyacetic Ester of the γ -Form of 1-Allyl-4-ethynyl-2,5-dimethyl-4-piperidinol (V). Fine magnesium turnings (0.5 g) were added to a solution of 4.2 g of the γ -form of 1-allyl-4-ethynyl-2,5-dimethyl-4-piperidinol (m.p. 92-93°) in 8 ml of dry benzene. Phenoxyacetyl chloride (10.2 g) was then added dropwise with stirring. The mixture was heated in a metal bath at 100-110° for five hours and then at 110-120° for five hours. Benzene and excess of the acid chloride were distilled off under reduced pressure, and the residue was dissolved in water, extracted with ether, and treated with sodium carbonate solution; the base liberated was repeatedly extracted with ether. The reaction product was not distilled, but was converted into its hydrochloride, which was recrystallized several times from 1:1 alcohol-acetone. The product (0.5 g) was the pure hydrochloride of the phenoxyacetic ester of the γ -form of 1-allyl-4-ethynyl-2,5-dimethyl-4-piperidinol, m.p. 166-167°.

Found %: C 66.10; 66.07; H 7.19; 7.19; N 4.08; 4.18; C 9.78; 9.62. $C_{20}H_{26}O_3NCl$.

Calculated %: C 65.99; H 7.20; N 3.85; Cl 9.76.

Benzoic Ester of the γ -Form of 1-(2-Butenyl)-4-ethynyl-2,5-dimethyl-4-piperidinol (VI). A mixture of 3.6 g of the hydrochloride of the γ -form of 1-(2-butenyl)-4-ethynyl-2,5-dimethyl-4-piperidinol (m.p. 208-209°), 5.5 g of benzoyl chloride, and 7 ml of dry pyridine was heated at 120-130° for 2.5 hours and left overnight. On the next day the precipitate was filtered off and washed with absolute alcohol. Two recrystallizations from alcohol gave 2.9 g of the hydrochloride of the benzoic ester of 1-(2-butenyl)-4-ethynyl-2,5-dimethyl-4-piperidinol, m.p. 211-212°.

Found %: C 69.22; 69.41; H 7.39; 7.13; N 4.11; 4.32; Cl 10.41; 10.26. $C_{20}H_{26}O_2NCl$.

Calculated %: C 69.05; H 7.54; N 4.02; Cl 10.20.

Benzoic Ester of the γ -Form of 4-Ethynyl-2,5-dimethyl-1-(3-methyl-2-butenyl)-4-piperidinol (VII). A mixture of 4 g of the hydrochloride of the γ -form of 4-ethynyl-2,5-dimethyl-1-(3-methyl-2-butenyl)-4-piperidinol (m.p. 205-206°), 5.6 g of benzoyl chloride, and 10 ml of dry pyridine was heated for 2.5 hours at 120-125°. The precipitate was filtered off, and two recrystallizations from absolute alcohol gave 3.5 g of the hydrochloride of the benzoyl ester of the γ -form of 4-ethynyl-2,5-dimethyl-1-(3-methyl-2-butenyl)-4-piperidinol, m.p. 217-218°.

Found %: C 69.69; 70.03; H 7.78; 7.72; N 4.06; 4.22; Cl 9.81; 9.88. $C_{21}H_{28}O_2NCl$.

Calculated %: C 69.60; H 7.80; N 3.87; Cl 9.81.

Phenoxyacetic Ester of the γ -Form of 4-Ethynyl-2,5-dimethyl-1-(3-methyl-2-butenyl)-4-piperidinol (VIII). A mixture of 4 g of the γ -form of 4-ethynyl-2,5-dimethyl-1-(3-methyl-2-butenyl)-4-piperidinol (m.p. 205-206°), 7.5 g of phenoxyacetyl chloride, and 10 ml of dry pyridine was heated for two hours at 100-110°. The usual treatment gave 0.5 g of the hydrochloride of the phenoxyacetic ester of the γ -form of 4-ethynyl-2,5-dimethyl-1-(3-methyl-2-butenyl)-4-piperidinol, m.p. 177-178° (from an alcohol-acetone mixture).

Found %: C 67.01; 67.07; H 7.73; 7.65; N 3.61; 3.72; Cl 9.29; 9.44. $C_{22}H_{30}O_3NCl$.

Calculated %: C 67.40; H 7.72; N 3.57; Cl 9.06.

Benzoic Ester of the β -Form of 4-Ethynyl-2,5-dimethyl-1-(3-methyl-2-butenyl)-4-piperidinol (VII). A mixture of 2.5 g of the hydrochloride of the β -form of 4-ethynyl-2,5-dimethyl-1-(3-methyl-2-butenyl)-4-piperidinol (m.p. 147-148°), 3.5 g of benzoyl chloride, and 5 ml of dry pyridine was heated for three hours at 120-125°; it was then cooled and diluted with 5 ml of dry ether. The precipitate of the hydrochloride of the ester (VII) was filtered off; after being recrystallized from absolute alcohol it melted at 206-207° (yield of pure hydrochloride 0.5 g).

Found %: C 69.91; 69.64; H 7.82; 7.83; N 3.96; 4.25; Cl 9.55; 9.73. $C_{21}H_{28}O_2NCl$.

Calculated %: C 69.60; H 7.80; N 3.87; Cl 9.81.

SUMMARY

1. 1-Alkenyl-2,5-dimethyl-4-piperidones were condensed with acetylene under a pressure of 5 atm with formation in high yield of the corresponding 1-alkenyl-4-ethynyl-2,5-dimethyl-4-piperidinols (I)-(III) in the form of mixtures of stereoisomers, which were separated into individual compounds by fractional crystallization of the hydrochlorides.

2. Esterification of the piperidinols (I)-(III) with benzoyl and phenoxyacetyl chlorides gave the benzoic and phenoxyacetic esters (IV)-(VIII), which were subjected to pharmacological tests for surface anesthesia. The most valuable of the esters examined was the benzoic ester of 1-(2-butenyl)-4-ethynyl-2,5-dimethyl-4-piperidinol (VI), which in 1% solution has the same activity as tetracaine (at the same concentration), but a toxicity that is less than that of tetracaine by a factor of almost 3.5.

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*Original Russian pagination. See C. B. Translation.

HETEROCYCLIC COMPOUNDS

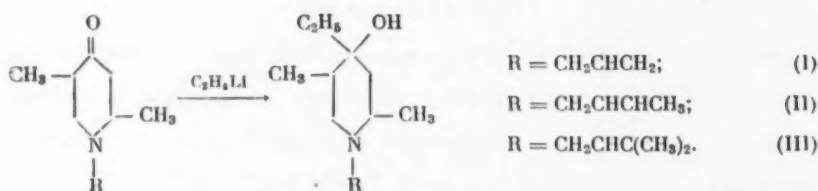
COMMUNICATION 59. SYNTHETIC ANESTHETICS

XX. SYNTHESIS OF BENZOIC AND PHENOXYACETIC ESTERS OF 1-ALKENYL-4-ETHYL-2,5-DIMETHYL-4-PIPERIDINOLS

I. N. Nazarov, A. Sh. Sharifkanov, and K. F. Danilova

In the preceding communication [1] we described a series of benzoic and phenoxyacetic esters of 1-alkenyl-4-ethynyl-2,5-dimethyl-4-piperidinols, certain members of which were found to have a powerful anesthetic action. Continuing this investigation, we decided to synthesize the benzoic and phenoxyacetic esters of 1-alkenyl-4-ethyl-2,5-dimethyl-4-piperidinols with the object of determining the effect of replacing ethynyl by ethyl on the physiological activities of these compounds.

The original 1-alkenyl-4-ethyl-2,5-dimethyl-4-piperidinols (I)-(III) were prepared in high yield (above 70%) by the condensation of ethyllithium [2, 3] with 1-alkenyl-2,5-dimethyl-4-piperidones, which were described in an earlier communication [4]:



As in the reaction with acetylene [1], the products of this reaction, 1-alkenyl-4-ethyl-4-piperidinols (I)-(III), were formed as noncrystallizing mixtures of stereoisomers.

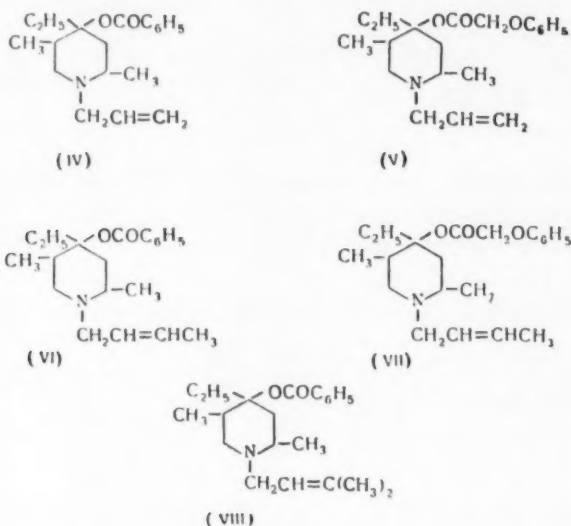
For the isolation of individual compounds the resulting mixtures of isomeric piperidinols (I)-(III) were converted into hydrochlorides. These were fractionally crystallized from alcohol, and the pure hydrochlorides isolated were reconverted into the free bases. In this way from the mixture of isomeric 1-allyl-4-ethyl-2,5-dimethyl-4-piperidinols (I) we isolated two stereoisomers: the γ -form of m.p. 64-65° (50% of the total mixture of isomers), and the liquid β -form (about 15% of the total mixture of isomers). From the mixture of isomeric 1-(2-butenyl)-4-ethyl-2,5-dimethyl-4-piperidinols (II) we succeeded in isolating only the crystalline γ -isomer of m.p. 37-38° (44% of the total mixture of isomers). From the mixture of isomeric 4-ethyl-2,5-dimethyl-1-(3-methyl-2-butenyl)-4-piperidinols (III) we again isolated only one isomer. In all the experiments the rest of the material remained in the form of an unresolved mixture of isomers.

By esterification of the 1-alkenyl-4-ethyl-2,5-dimethyl-4-piperidinols (I)-(III) with benzoyl and phenoxyacetyl chlorides we prepared the corresponding benzoic and phenoxyacetic esters (IV)-(VIII).

The benzoic and phenoxyacetic esters of 1-alkenyl-4-ethyl-2,5-dimethyl-4-piperidinols (IV)-(VIII) were tested in the form of their hydrochlorides for surface anesthesia by Renier's method in Professor M. D. Mashkovskii's laboratory (S. Ordzhonikidze VNIKhFI)*. The anesthetic effects of the esters synthesized were estimated by comparison

* Transliteration of Russian - Publisher's note.

with those of procaine and tetracaine. All the esters examined were highly active, particularly the phenoxy-acetic ester of 1-(2-butenyl)-4-ethyl-2,5-dimethyl-4-piperidinol (VII), which at a concentration of 0.05% has an anesthetic effect equal to that of tetracaine at a concentration of 0.25%; however, its toxicity is also higher than that of tetracaine (by a factor of about 2). The results of the tests are given in the table.



EXPERIMENTAL

1-Allyl-4-ethyl-2,5-dimethyl-4-piperidinol (I). A three-necked flask fitted with stirrer, reflux condenser, and tube for the passage of nitrogen (the synthesis was carried out in an atmosphere of dry nitrogen) was charged with 800 ml of petroleum ether (b.p. 36-40°) and 14 g of finely chopped lithium, and with stirring over a period of 90 minutes a solution of 130 g of ethyl bromide in 400 ml of petroleum ether was added dropwise. The mixture was heated at a gentle boil until the lithium dissolved completely (two hours). The resulting ethereal solution of ethyllithium was cooled to -6°, and a solution of 67 g of 1-allyl-2,5-dimethyl-4-piperidone (b.p. 76° (2 mm); n_D^{20} 1.4745) [4] in 100 ml of petroleum ether was added dropwise; the mixture was then heated with stirring for two hours. The product was hydrolyzed by addition of dilute (1 : 2) hydrochloric acid with cooling; the ethereal layer was separated and washed twice with dilute hydrochloric acid. The combined acidic aqueous solution was treated with alkali, and the base liberated was separated, extracted repeatedly with ether, dried, and vacuum-fractionated. We then obtained 11.4 g of unchanged piperidone and 57.5 g (about 72%) of a mixture of stereo-isomeric 1-allyl-4-ethyl-2,5-dimethyl-4-piperidinols in the form of a thick noncrystallizing liquid; b.p. 82-90° (2 mm); n_D^{20} 1.4872; d_4^{20} 0.9448; found MR 60.05; calculated MR 60.11.

Found %: N 7.20; 7.33. $C_{12}H_{23}ON$. Calculated %: N 7.09.

The mixture of isomeric piperidinols (81 g) was converted into the hydrochlorides. By fractional crystallization from absolute alcohol the following two pure hydrochlorides of 1-allyl-4-ethyl-2,5-dimethyl-4-piperidinols were isolated:

1) The hydrochloride of the γ -form, m.p. 179-180° (48 g, i.e., 50% of the total mixture of isomers).

Found %: Cl 15.10; 15.01. $C_{12}H_{24}ONCl$. Calculated %: Cl 15.18.

The hydrochloride was reconverted into the base by treatment with alkali; this gave the crystalline γ -isomer, m.p. 64-65° (from petroleum ether).

Found %: N 7.16; 7.20. $C_{12}H_{23}ON$. Calculated %: N 7.09.

2) The hydrochloride of the β -form, m.p. 162-163° (15 g, i.e., 15% of the total mixture of isomers).

Results of Pharmacological Tests on the Esters

* Irritates the cornea.

Found %: Cl 15.23; 15.41. $C_{12}H_{24}ONCl$. Calculated %: Cl 15.18.

The hydrochloride was reconverted into the base; this gave the liquid β -isomer; b.p. 96-97° (2 mm); n_D^{20} 1.4839; d_4^{20} 0.93945; found MR 60.08; calculated MR 60.11.

Found %: N 7.00; 7.11. $C_{12}H_{23}ON$. Calculated %: N 7.09.

A mixture of the hydrochloride of the γ -form (m.p. 179-180°) with the hydrochloride of the β -form (m.p. 162-163°) melted at 137-143°.

1-(2-Butenyl)-4-ethyl-2,5-dimethyl-4-piperidinol (II). A solution of 91.2 g of 1-(2-butenyl)-2,5-dimethyl-4-piperidone [b.p. 87-89° (2 mm); n_D^{20} 1.4761] [4] in 100 ml of petroleum ether was added dropwise to a solution of ethyllithium prepared as described above from 14 g of lithium, 114 g of ethyl bromide, and 1100 ml of petroleum ether, the mixture was heated for two hours, and the product was then hydrolyzed with dilute (1 : 2) hydrochloric acid and treated in the usual way. Vacuum fractionation gave 17.5 g of unchanged piperidone, 18 g of intermediate fraction (b.p. 92-99° (2 mm); n_D^{20} 1.4805), and 47.5 g of a mixture of stereoisomeric 1-(2-butenyl)-4-ethyl-2,5-dimethyl-4-piperidinols in the form of a noncrystallizing liquid; b.p. 99-109° (2 mm); n_D^{20} 1.4885; d_4^{20} 0.9482; found MR 64.26; calculated MR 65.05.

Found %: N 6.55; 6.88. $C_{13}H_{25}ON$. Calculated %: N 6.62.

By fractional crystallization from absolute alcohol, 84 g of the mixture of isomeric piperidinols gave 43 g (44% of the total mixture of isomers) of the pure hydrochloride of the γ -form, m.p. 169-170°.

Found %: Cl 14.56; 14.70. $C_{13}H_{26}ONCl$. Calculated %: 14.62.

The hydrochloride was reconverted into the base; this gave the crystalline γ -isomer, m.p. 87-88° (from petroleum ether).

Found %: N 6.74; 6.84. $C_{13}H_{25}ON$. Calculated %: N 6.62.

The residue remaining after the isolation of the crystalline γ -isomer yielded liquid piperidinol; b.p. 102-105° (3 mm); n_D^{20} 1.4855.

Found %: N 6.88; 6.99. $C_{13}H_{25}ON$. Calculated %: N 6.62.

The hydrochloride of this substance was also a noncrystallizing liquid.

4-Ethyl-2,5-dimethyl-1-(3-methyl-2-butenyl)-4-piperidinol (III). A solution of 19.5 g of 2,5-dimethyl-1-(3-methyl-2-butenyl)-4-piperidone [b.p. 84-86° (2 mm); n_D^{20} 1.4810] [4] in 10 ml of dry ether was added over a period of 40 minutes to a cooled, stirred solution of ethyllithium prepared from 5.3 g of lithium and 45.84 g of ethyl bromide in 130 ml of dry ether. The reaction mixture was then left overnight (in an atmosphere of dry nitrogen). On the next day the mixture was heated for five hours. The reaction product was treated in the usual way and extracted with ether. The extract was dried, and ether was distilled off. Vacuum distillation of the residue gave 15 g (about 66%) of a mixture of stereoisomeric 4-ethyl-2,5-dimethyl-1-(3-methyl-2-butenyl)-4-piperidinols as a liquid of b.p. 111-113° (2 mm); n_D^{20} 1.4900; d_4^{20} 0.9414; found MR 69.16; calculated MR 69.39.

Found %: N 6.46; 6.36. $C_{14}H_{27}ON$. Calculated %: N 6.22.

Dry hydrogen chloride was passed into a solution of 18.3 g of the mixture of isomeric piperidinols in acetone; this gave 7.17 g of crystalline hydrochlorides, m.p. 145-157°. Fractional crystallization of the hydrochlorides from acetone gave 1.9 g of the pure hydrochloride of the γ -form of 4-ethyl-2,5-dimethyl-1-(3-methyl-2-butenyl)-4-piperidinol, m.p. 187-188°.

Found %: N 5.03; 5.28; Cl 14.85. $C_{14}H_{28}ONCl$. Calculated %: N 5.35; Cl 13.95.

The hydrochloride of m.p. 187-188° was reconverted into the base; this gave a liquid piperidinol; b.p. 124° (4 mm); n_D^{20} 1.4915.

After removal of acetone from the mother liquor, a noncrystallizing residue of hydrochlorides remained and was reconverted into the base; this gave a 4-ethyl-2,5-dimethyl-1-(3-methyl-2-butenyl)-4-piperidinol of b.p. 120-123° (3 mm); n_D^{20} 1.4900.

Benzoic Ester of the γ -Form of 1-Allyl-4-ethyl-2,5-dimethyl-4-piperidinol (IV). A mixture of 3.5 g of the hydrochloride of the γ -form of 1-allyl-4-ethyl-2,5-dimethyl-4-piperidinol (m.p. 179-180°), 6.5 g of benzoyl chloride, and 8 ml of dry pyridine was heated for six hours at 125-126°. The pyridine and excess of benzoyl chloride were distilled off under reduced pressure, and the residue was dissolved in water. The solution was extracted with ether and then treated with sodium carbonate; the oil formed was separated, and the aqueous solution was extracted repeatedly with ether. The combined ether solution was dried with sodium sulfate; ether was driven off. Vacuum distillation of the residue gave 1.5 g (33.3%) of the benzoic ester of the γ -form of 1-allyl-4-ethyl-2,5-dimethyl-4-piperidinol in the form of a thick liquid; b.p. 140-150° (1 mm); n_D^{20} 1.5190.

Found %: 4.84; 4.81. $C_{19}H_{27}O_2N$. Calculated %: 4.64.

The benzoic ester was converted into its hydrochloride, m.p. 125-126° (from alcohol).

Found %: C 67.47; 67.21; H 8.43; 8.25; N 4.17; 4.18; Cl 9.96; 9.90. $C_{19}H_{26}O_2NCl$.

Calculated %: C 67.53; H 8.35; N 4.15; Cl 10.51.

Phenoxyacetic Ester of the γ -Form of 1-Allyl-4-ethyl-2,5-dimethyl-4-piperidinol (V). A mixture of 3 g of the γ -form of 1-allyl-4-ethyl-2,5-dimethyl-4-piperidinol (m.p. 64-65°), 6.3 g of phenoxyacetyl chloride, 0.5 g of magnesium turnings, and 6 ml of dry benzene was heated at 90-95° for ten hours. Benzene and excess of the acid chloride were removed by vacuum distillation over a boiling water bath, the residue was dissolved in water, and the aqueous solution was extracted with ether and treated with sodium carbonate. The base liberated was extracted with ether, and the ethereal solution was dried with sodium sulfate. Vacuum fractionation of the product gave 1.8 g (36.6%) of the phenoxyacetic ester of the γ -form of 1-allyl-4-ethyl-2,5-dimethyl-4-piperidinol as a thick liquid, b.p. 150-155° (1 mm). This ester was converted into its hydrochloride, m.p. 154-155° (from alcohol-acetone mixture).

Found %: C 65.22; 65.61; H 8.13; 8.10; N 3.88; 4.02; Cl 10.44; 10.64. $C_{20}H_{30}O_3NCl$.

Calculated %: C 65.28; H 8.29; N 3.80; Cl 9.64.

Benzoic Ester of the β -Form (Liquid Isomer) of 1-Allyl-4-ethyl-2,5-dimethyl-4-piperidinol (IV). A mixture of 3 g of the β -form of 1-allyl-4-ethyl-2,5-dimethyl-4-piperidinol (n_D^{20} 1.4839), 3 g of benzoyl chloride, and 15 ml of dry pyridine was heated at 105-107° for two hours. On the next day a further 3 g of benzoyl chloride was added, and the mixture was heated at 135-140° for six hours. After suitable treatment of the reaction product and vacuum fractionation of the liberated base, we obtained 2 g (44.5%) of the benzoic ester of the β -form of 1-allyl-4-ethyl-2,5-dimethyl-4-piperidinol as a thick liquid; b.p. 142-145° (3 mm); n_D^{20} 1.5192.

Found %: N 4.73; 5.04. $C_{19}H_{27}O_2N$. Calculated %: N 4.64.

Its hydrochloride had m.p. 167-168°. A mixture with the hydrochloride of the original piperidinol (m.p. 162-163°) melted at 135-145°.

Found %: Cl 10.61; 10.66. $C_{19}H_{26}O_2NCl$. Calculated %: Cl 10.51.

Benzoic Ester of the γ -Form of 1-(2-Butenyl)-4-ethyl-2,5-dimethyl-4-piperidinol (VI). A mixture of 3.7 g of the hydrochloride of the γ -form of 1-(2-butenyl)-4-ethyl-2,5-dimethyl-4-piperidinol (m.p. 169-170°), 6.3 g of benzoyl chloride, and 7 ml of dry pyridine was heated at 125-130° for seven hours. After suitable treatment of the reaction product the base liberated was vacuum distilled. We obtained 2.3 g (50%) of the benzoic ester of the γ -form of 1-(2-butenyl)-4-ethyl-2,5-dimethyl-4-piperidinol as a thick liquid, b.p. 140-146° (1 mm).

Found %: N 4.43; 4.49. $C_{18}H_{25}O_2N$. Calculated %: N 4.43.

Its hydrochloride had m.p. 161-162° (from absolute alcohol). A mixture with the hydrochloride of the original piperidinol melted at 139-159°.

Found %: C 68.21; 68.55; H 8.58; 8.59; N 4.28; 4.32; Cl 9.98; 10.18. $C_{20}H_{30}O_2NCl$.

Calculated %: C 68.28; H 8.59; N 3.97; Cl 10.01.

Phenoxyacetic Ester of the γ -Form of 1-(2-Butenyl)-4-ethyl-2,5-dimethyl-4-piperidinol (VII). A mixture of 3.2 g of the γ -form of 1-(2-butenyl)-4-ethyl-2,5-dimethyl-4-piperidinol (m.p. 37-38°), 6.5 g of phenoxyacetyl chloride, 0.5 g of magnesium turnings, and 6 ml of dry benzene was heated at 90-95° for ten hours. After suitable treatment of the reaction product and vacuum fractionation of the liberated base, we obtained 1.7 g (about 33%)

of the phenoxyacetic ester of the γ -form of 1-(2-butenyl)-4-ethyl-2,5-dimethyl-4-piperidinol as a thick liquid; b.p. 145-150° (1 mm); n_D^{20} 1.5115.

Found %: N 4.26; 4.24. $C_{21}H_{31}O_3N$. Calculated %: N 4.05.

Its hydrochloride had m.p. 148-149° (from alcohol).

Found %: C 65.86; 65.72; H 8.32; 8.32; N 3.64; 3.70; Cl 10.12; 10.13. $C_{21}H_{32}O_3NCl$.

Calculated %: C 66.04; H 8.44; N 3.66; Cl 9.29.

Benzoic Ester of Liquid 1-(2-Butenyl)-4-ethyl-2,5-dimethyl-4-piperidinol (VI). A mixture of 3.2 g of 1-(2-butenyl)-4-ethyl-2,5-dimethyl-4-piperidinol (n_D^{20} 1.4855), 6 g of benzoyl chloride, and 10 ml of dry pyridine was heated at 100-102° for two hours and then at 128-132° for eight hours. After suitable treatment of the reaction mixture and vacuum distillation of the liberated base, we obtained 2 g (42.5%) of the benzoic ester of 1-(2-butenyl)-4-ethyl-2,5-dimethyl-4-piperidinol; b.p. 145-150° (2 mm); n_D^{20} 1.5212.

Found %: N 4.61; 4.83. $C_{20}H_{29}O_2N$. Calculated %: N 4.43.

Its hydrochloride was a noncrystallizing liquid.

Benzoic Esters of 4-Ethyl-2,5-dimethyl-1-(3-methyl-2-butenyl)-4-piperidinols (VIII). 1. A mixture of 0.9 g of the γ -form of 4-ethyl-2,5-dimethyl-1-(3-methyl-2-butenyl)-4-piperidinol (b.p. 124° (4 mm); n_D^{20} 1.4915), 1.2 g of benzoyl chloride, and 3 ml of dry pyridine was heated at 125-130° for five hours. A further 1 g of benzoyl chloride was added to the cooled mixture, which was again heated at 125-180° for ten hours; when cool it was diluted with ether. The precipitate was filtered off, and recrystallization from benzene gave 0.5 g (35%) of the hydrochloride of the benzoic ester of the γ -form of 4-ethyl-2,5-dimethyl-1-(3-methyl-2-butenyl)-4-piperidinol, m.p. 172-173°.

Found %: N 3.71; 3.78; Cl 10.11; 10.46. $C_{21}H_{32}O_2NCl$. Calculated %: N 3.83; Cl 9.70.

2. Benzoyl chloride (7.2 g) was added to a solution of 6 g of the liquid mixture of isomeric piperidinols (b.p. 120-123° (3 mm); n_D^{20} 1.4900) in 10 ml of pyridine. The mixture was heated at 125-130° for five hours. The reaction product was precipitated with dry ether, and two crystallizations from acetone then gave 2.5 g (26%) of the hydrochloride of the benzoic ester of 4-ethyl-2,5-dimethyl-1-(3-methyl-2-butenyl)-4-piperidinol, m.p. 193-194°.

Found %: N 3.75; 3.89; Cl 9.63; 9.40. $C_{21}H_{32}O_2NCl$. Calculated %: N 3.83; Cl 9.70.

SUMMARY

1. By the action of ethyllithium on 1-alkenyl-2,5-dimethyl-4-piperidones the corresponding 1-alkenyl-4-ethyl-2,5-dimethyl-4-piperidinols (I)-(III) were obtained in the form of mixtures of stereoisomers, which were separated into the individual compounds by fractional crystallization of their hydrochlorides.

2. The benzoic and phenoxyacetic esters of 1-alkenyl-4-ethyl-2,5-dimethyl-4-piperidinols (IV)-(VIII) were synthesized and were investigated pharmacologically for surface anesthesia; they were found to be highly active. The phenoxyacetic ester of the γ -form of 1-(2-butenyl)-4-ethyl-2,5-dimethyl-4-piperidinol (VII) is much more active than tetracaine, but is almost twice as toxic. The activity of the benzoic ester of the γ -form of 1-allyl-4-ethyl-2,5-dimethyl-4-piperidinol (IV) in 1% solution is equal to that of tetracaine at the same concentration, but its toxicity is less than that of tetracaine by a factor of 3.5.

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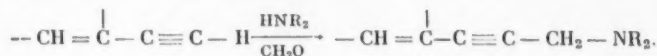
ACETYLENE DERIVATIVES

COMMUNICATION 181. HYDRATION OF 4-ALKEN-2-YNYLAMINES INTO UNSATURATED

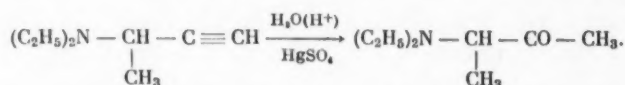
β -AMINO KETONES

I. N. Nazarov and E. A. Mistriukov

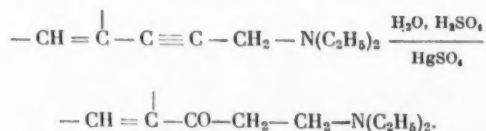
In a previous investigation we studied the Mannich reaction with hydrocarbons derived from 1-buten-3-yne and so obtained various 4-alken-2-ynylamines in high yield:



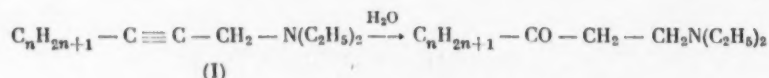
It was of interest to study the hydration of these amines, for the unsaturated β -amino ketones then formed may be valuable intermediate products for the synthesis of physiologically active substances and, in particular, anesthetics. There are no references in the literature to hydration of 4-alken-2-ynylamines. The usual methods for the hydration of the triple bond did not give satisfactory results when applied to the 4-alken-2-ynylamines described in the previous communication [1]. Thus, when N,N-diethyl-4-methyl-4-hexen-2-ynylamine was heated in 10-20% sulfuric acid in presence of mercuric sulfate or in acetic acid containing mercuric acetate, the amine was recovered unchanged. When the present work was started, only one example was known of the hydration of an acetylenic amine, i.e., the hydration of N,N-diethyl-1-methyl-2-propynylamine into the corresponding amino ketone [2]



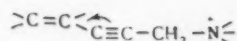
This hydration was effected by heating 1 mole of amine with 5 moles of 88% sulfuric acid containing mercuric sulfate at 100°. An attempt to hydrate 4-alken-2-ynylamines under these conditions was not successful, for considerable resinification occurred both during the hydration and in the subsequent neutralization of the large amount of sulfuric acid. Only after careful investigation did we succeed in finding conditions for the hydration of 4-alken-2-ynylamines. It was shown by special experiments that aqueous ammonia does not add to an appreciable extent to substituted α, β -unsaturated ketones. This enabled us to use aqueous ammonia for the neutralization of the reaction mixture and so avoid resinification (ammonia does not promote the condensation of the amino ketones). Optimum conditions for the hydration of 4-alken-2-ynylamines were found to be as follows: a mixture of 1 mole of amine, 1 mole of sulfuric acid (2 moles for some amines), 2.5 moles of water, and about 4 g of mercuric sulfate is heated at 60-70° for 1-2 hours, and the mixture is then neutralized with 13 N aqueous ammonia. Under these conditions the corresponding amino ketones are obtained in 80% yield.



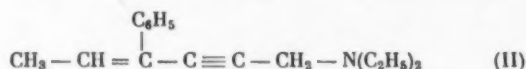
It must be noted that deprature from these conditions results in a sharp fall in the yield of hydration product. Thus, if the amount of sulfuric acid is reduced by one-third, or the amount of water is doubled without alteration in the relative amounts of amine and sulfuric acid, then hydration stops altogether. Moreover, reproducible results could not be obtained until it was discovered that traces of impurity in the original amine can greatly retard the hydration process, probably by poisoning the mercury catalyst. A recent paper on the hydration of some 2-alkynylamines (I) [3]



enables us to compare the conditions for the hydration of these acetylenic amines with those for the hydration of 4-alken-2-ynylamines. The comparison shows that the triple bond in acetylenic amines of the type (I) is hydrated at lower concentrations of sulfuric acid than the triple bond in 4-alken-2-ynylamines. It is probable that the double bond of 4-alken-2-ynylamines has a certain inhibiting action due to lowering of the nucleophilic character of the triple bond by conjugation:

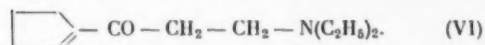
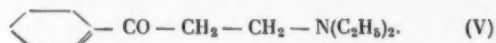
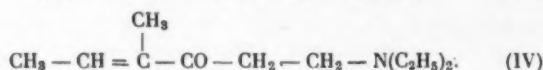
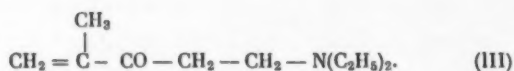


We did not succeed in effecting the hydration of N,N-diethyl-4-phenyl-4-hexen-2-ynylamine (II).

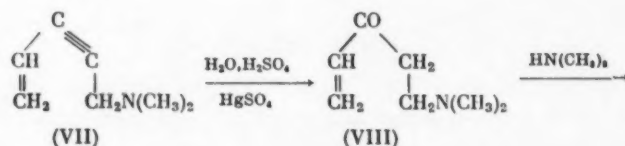


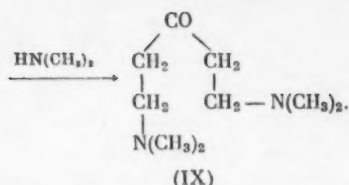
Under the conditions under which the other 4-alken-2-ynylamines (with aliphatic substituents) pass smoothly into the corresponding amino ketones, the amine (II) remains quite unchanged. In this case the nucleophilic character of the triple bond is still further weakened by the introduction of phenyl. It is possible that the phenyl group also shows steric hindrance.

Thus, by the hydration of aminomethyl derivatives of hydrocarbons derived from 1-buten-3-yne we prepared the following unsaturated β -amino ketones: 5-diethylamino-2-methyl-1-penten-3-one (III), 1-diethylamino-4-methyl-4-hexen-3-one (IV), 1-cyclohexen-1-yl 2-diethylaminoethyl ketone (V), and 1-cyclopenten-1-yl 2-diethylaminoethyl ketone (VI):



In the case of the hydration of the amine derived from unsubstituted 1-buten-3-yne (VII) [4], an unstable unsaturated β -amino ketone (VIII) is formed and may be isolated from the reaction mixture in the form of the more stable saturated β, β' -diamino ketone (IX), which is formed by addition of a molecule of secondary amine to the unsaturated amino ketone (VIII):





The diamino ketone (IX) resinifies fairly rapidly when allowed to stand, but the amino ketones (III)-(VI) change very slowly during storage. The structure of these amino ketones was confirmed by their ready scission into the dialkylamine and the corresponding divinyl ketone on heating and also by some other reactions, which will be described in future communications.

EXPERIMENTAL

The 4-alken-2-ynylamines used in the hydration reaction were prepared from 1-buten-3-yne hydrocarbons by the Mannich reaction and were described in a previous paper [1].

5-Diethylamino-2-methyl-1-penten-3-one (III). A flask fitted with thermometer, dropping funnel, and powerful stirrer was charged with 102 g (0.676 mole) of N,N-diethyl-4-methyl-4-penten-2-ynylamine. With water cooling and vigorous stirring a solution of 26 ml of water in 41.3 ml (0.743 mole) of concentrated sulfuric acid (sp.gr. 1.84) was added gradually to the amine, and then 3 g of finely ground mercuric sulfate was added. The mixture was stirred for 20 minutes at room temperature, after which it was heated carefully until an exothermic reaction set in (about 60°); the application of heat was immediately stopped, and the temperature was maintained at not above 63-68° by cooling with cold water. When the exothermic reaction stopped, the reaction mixture was heated at 60° for 2 hours 15 minutes (after the first hour a further 0.5 g of mercuric sulfate was added). The product was diluted with 16 ml of water and 150 ml of ether, neutralized with 116 ml of 13 N aqueous ammonia with vigorous stirring and cooling with ice and salt (temperature not above 8°), extracted with ether, dried with magnesium sulfate, and vacuum-fractionated. The product, amounting to 85.7 g (75%), was 5-diethylamino-2-methyl-1-penten-3-one (III); b.p. 64-66° (1.5 mm); n_D^{20} 1.4565.

Found %: C 70.99; H 11.28; N 8.40. $\text{C}_{10}\text{H}_{19}\text{NO}$. Calculated %: C 71.0; H 11.2; N 8.30.

1-Cyclopenten-1-yl 2-Diethylaminoethyl Ketone (VI). From 185 g (1.04 moles) of 3-(1-cyclopenten-1-yl)-N,N-diethyl-2-propynylamine, 59.2 ml (1.04 moles) of concentrated sulfuric acid (sp.gr. 1.84), and 39 ml of water we prepared, as in the previous experiment, an acid sulfate, which, after addition of ground mercuric sulfate and stirring for 20 minutes at 20-25°, was heated cautiously. At 65° an exothermic reaction set in. The temperature was kept below 75° by cooling with cold water. When the exothermic reaction stopped, the mixture was heated at 75° for 90 minutes in all (from moment of attainment of 70°); 30 minutes before the end of the reaction a further 1 g of mercuric sulfate was added. The product was diluted with 100 ml of water and neutralized with 178 ml of 13 N aqueous ammonia as in the previous experiment. The base was extracted with ether, the extract was dried with magnesium sulfate, and ether was removed under reduced pressure. The residue consisted of fairly pure 1-cyclopenten-1-yl 2-diethylaminoethyl ketone (VI), which was used in further work without purification, because on distillation the product was to a large extent decomposed into 1-cyclopenten-1-yl vinyl ketone and diethylamine.

The picrate of 1-cyclopenten-1-yl 2-diethylaminoethyl ketone has m.p. 113-114° (from alcohol).

Found %: C 51.10; H 5.70; N 13.17. $\text{C}_{18}\text{H}_{24}\text{N}_4\text{O}_8$. Calculated %: C 50.90; H 5.66; N 13.20.

Hydration of N,N-Dimethyl-4-penten-2-ynylamine (VII). From 30 g of N,N-dimethyl-4-penten-2-ynylamine [4] (0.275 mole), 15.6 ml of 94% sulfuric acid (0.275 mole) and 15 ml of water we prepared an acid sulfate, which was stirred with 2 g of mercuric sulfate for 20 minutes at room temperature; it was then gradually heated to 48° over a period of 15 minutes. This temperature (48-50°) was maintained for 75 minutes. With vigorous stirring and cooling with ice and salt (temperature not above 8°), 110 ml of 8.38 N aqueous dimethylamine was then added. After saturation of the aqueous layer with ammonium sulfate, the base was extracted with ether, dried with potassium carbonate, and distilled. Up to 35° (12 mm) about 4 g of the original amine came over, and at 80-82° (3 mm) we collected 14.48 g (31%) of 1,5-bisdimethylamino-3-pentanone (IX); n_D^{20} 1.4500. Since the diamino ketone (IX) changed rapidly with keeping, it was converted immediately into the dihydrochloride by addition of alcoholic

hydrogen chloride to its alcoholic solution. The dihydrochloride of the diamino ketone (IX) has m.p. 190.5-191° (from alcohol).

Found %: C 44.28; H 9.05; N 10.83; Cl 28.62. $C_9H_{22}N_2OCl_2$. Calculated %: C 44.2; H 9.0; N 11.4; Cl 28.9.

1-Diethylamino-4-methyl-4-hexen-3-one (IV). In this case, and also in the experiment described below, two moles of sulfuric acid were taken to every one mole of 4-alken-2-ynylamine. With water cooling (temperature not above 55-60°) a solution of 12 ml of water in 34.2 ml (0.616 mole) of 94% sulfuric acid was added to 51.02 g (0.308 mole) of N,N-diethyl-4-methyl-4-hexen-2-ynylamine. The solution was cooled to 20-25°, 1.5 g of ground mercuric sulfate was added, and the mixture was stirred until this was dissolved; it was then heated gradually to about 60°, at which temperature an exothermic reaction set in (in some cases fairly rapid spontaneous heating occurred). In the course of 50 minutes the temperature of the reaction mixture was maintained at 90-95°, first by cooling with cold water and later by heating in a water bath. The product was diluted with 50 ml of water, and the free amino ketone base was liberated by addition of 93 ml of 13 N aqueous ammonia, as indicated in the previous experiments. The amino ketone so obtained can be used without purification. In order to obtain pure 1-diethylamino-4-methyl-4-hexen-3-one (IV), the unpurified amino ketone was carefully distilled at a residual pressure of 1-2 mm from a metal bath at 130°. Considerable decomposition then occurred; 10 ml of diethylamine was therefore added to the distillate and, when the evolution of heat ceased, the amino ketone was redistilled. We then obtained 44.21 g (78%) of 1-diethylamino-4-methyl-4-hexen-3-one (IV); b.p. 77-79° (0.5 mm); n_D^{20} 1.4670.

Found %: N 7.54. $C_{11}H_{21}NO$. Calculated %: N 7.65.

1-Cyclohexen-1-yl 2-Diethylaminoethyl Ketone (V). From 100 g (0.565 mole) of 3-(1-cyclohexen-1-yl)-N,N-diethyl-2-propynylamine, 64 ml (1.13 moles) of 94% sulfuric acid, and 23 ml of water we obtained a solution of the acid sulfate. This solution was stirred in presence of 2 g of ground mercuric sulfate, and the temperature rapidly rose (in about 15 minutes) to 70° with the heat of reaction. Until the exothermic reaction stopped (about 30 minutes), the temperature was maintained at 69-72° by water cooling; the mixture was then heated at 80-83° for 40 minutes, diluted with 100 ml of water, neutralized with 200 ml of 13 N aqueous ammonia, and extracted with ether, as in the previous experiments. We obtained 108.2 g of unpurified 1-cyclohexen-1-yl 2-diethylaminoethyl ketone containing more than 90% of the main product. Pure 1-cyclohexen-1-yl 2-diethylaminoethyl ketone (V) was prepared by addition of diethylamine to the distillate obtained, distilling the unpurified amino ketone, and removal of the excess of diethylamine under reduced pressure. The yield of pure amino ketone (V) was 81%; n_D^{20} 1.4910.

Found %: C 74.48; H 11.01; N 6.60. $C_{13}H_{23}NO$. Calculated %: C 74.46; H 11.00; N 6.70.

Its picrate had m.p. 91-92° (from alcohol).

Attempt at the Hydration of N,N-Diethyl-4-phenyl-4-hexen-2-ynylamine. When a mixture of 23 g (0.101 mole) of N,N-diethyl-4-phenyl-4-hexen-2-ynylamine, 11.2 ml (0.202 mole) of 94% sulfuric acid, 4 ml of water, and 0.5 g of mercuric sulfate was heated under the conditions of the previous experiment, 18.3 g of the original amine was recovered unchanged; it was identified by its boiling point and refractive index, and also by the absence of any depression of the melting point of its picrate in admixture with the picrate of the original amine.

SUMMARY

The conditions were found for the hydration of 4-alken-2-ynylamines, and by this means several previously inaccessible β -amino ketones were synthesized in high yield; such amino ketones are of interest for the synthesis of 4-piperidones and of some physiologically active compounds, in particular anesthetics.

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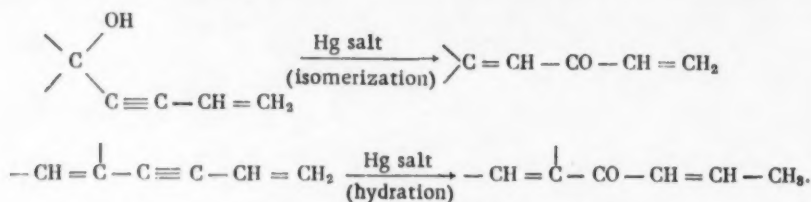
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ACETYLENE DERIVATIVES

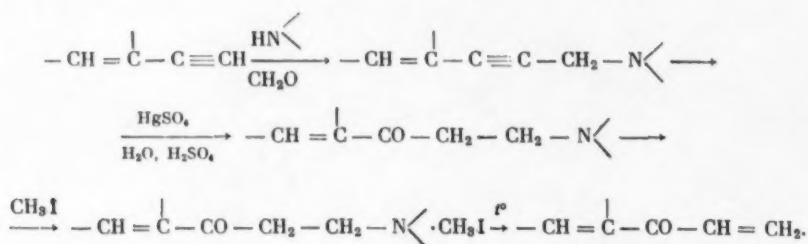
COMMUNICATION 182. NEW METHOD OF SYNTHESIZING DIVINYL KETONES BY THE DEGRADATION OF METHIODIDES OF ALKENYL 2-DIETHYLAMINOETHYL KETONES

I. N. Nazarov and E. A. Mistriukov

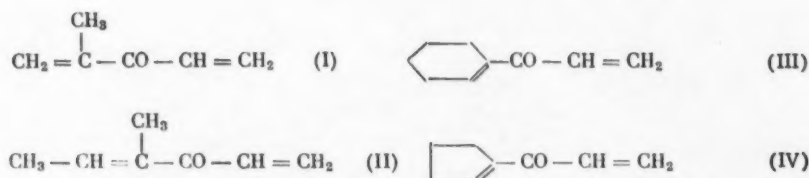
In our laboratory we have developed two methods for the preparation of divinyl ketones: the isomerization of 3-buten-1-ynylmethanols [1] and the hydration of hydrocarbons derived from 1,5-hexadien-3-yne [2]:



We now describe a third method for the preparation of divinyl ketones: degradation of alkenyl 2-dialkylaminoethyl ketones, which are described in a previous paper [3] and are prepared by the hydration of 4-alken-2-ynylamines [4]. The whole series of reactions is illustrated by the following scheme:



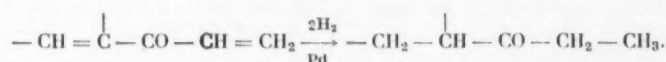
We investigated the pyrolysis of various salts of alkenyl 2-dialkylaminoethyl ketones (hydrochlorides, sulfates, boron trifluoride addition products, methiodides); the best results were obtained by the degradation of the methiodides, which gave the corresponding alkenyl vinyl ketones in about 70% yield. By this method we prepared 2-methyl-1,4-pentadien-3-one (I), 4-methyl-1,4-hexadien-3-one (II), 1-cyclohexen-1-yl vinyl ketone (III), and 1-cyclopenten-1-yl vinyl ketone (IV):



The pyrolysis of sulfates and hydrochlorides of alkenyl 2-diethylaminoethyl ketones proceeded with greater difficulty, and the alkenyl vinyl ketones formed polymerized extremely readily. It is probable that in the pyrolysis of the methiodides small amounts of iodine compounds (and free iodine), which passed into the distillate, acted as polymerization inhibitors.

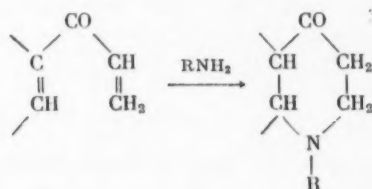
There are references in the literature to the low-temperature pyrolysis of the complexes formed by Mannich bases with boron trifluoride [5]. In our case this method was found to be unsuitable, for the complexes formed by boron trifluoride with the unsaturated β -amino ketones are degraded much less readily than the corresponding methiodides or sulfates.

There can be no doubt about the structures of the divinyl ketones (I)-(IV), because they are determined by the method of preparation. 1-Cyclohexen-1-yl vinyl ketone (III) was prepared previously by Braude and Coles [6] by the action of 1-cyclohexen-1-yl lithium on acrolein, followed by oxidation of the resulting alcohol with manganese dioxide; their values of its constants are in accord with ours. Our method is much simpler than Braude's and is more suitable for large-scale preparations. In the catalytic hydrogenation of the divinyl ketones (I)-(IV) two molecular proportions of hydrogen are absorbed and the corresponding saturated ketones are formed:



All the alkenyl vinyl ketones (I)-(IV) are pungently smelling mobile liquids which polymerize rapidly to a glassy mass.

Because of their reactivity, divinyl ketones are of great interest, both for theoretical investigations and for the synthesis of various new aliphatic, carbocyclic, and heterocyclic compounds. In particular, by a method developed in our laboratory [7] the divinyl ketones (I)-(IV) can be readily converted into previously inaccessible 4-piperidones, which are of great interest for the synthesis of new highly active anesthetics (analgetics):



EXPERIMENTAL

1-Cyclohexen-1-yl Vinyl Ketone (III). In a flask fitted with reflux condenser, 12.2 g (0.058 mole) of 1-cyclohexen-1-yl 2-diethylaminoethyl ketone [3], 5 ml (0.08 mole) of methyl iodide, and 30 ml of ether were mixed rapidly together. The mixture was left overnight, and on the next day the ether and excess of methyl iodide were driven off under reduced pressure. The oily methiodide was distilled at a residual pressure of 10 mm with gradual heating in a metal bath to 180-190°. After 15-20 minutes the divinyl ketone ceased coming over. Ether containing pyrogallol was added to the distillate, and the ethereal solution was washed with water, dried with magnesium sulfate, and fractionated. The product, amounting to 5 g (62%), was 1-cyclohexen-1-yl vinyl ketone; b.p. 91-94° (10 mm); n_D^{20} 1.5148. For this ketone Braude gives b.p. 47-48° (0.1 mm) and n_D^{25} 1.5100 [6].

Found %: C 79.37; H 9.02. $\text{C}_9\text{H}_{12}\text{O}$. Calculated %: C 79.41; H 8.83.

1-Cyclopenten-1-yl Vinyl Ketone (IV). Methyl iodide (14 ml, i.e., 0.225 mole) was added to a solution of 29.3 g (0.15 mole) of unpurified 1-cyclopenten-1-yl 2-diethylaminoethyl ketone [3] in 30 ml of ether. An exothermic reaction set in immediately, and when this stopped the reaction mixture was heated for one hour at 45-55°. Ether and excess of methyl iodide were removed under reduced pressure, and the residue was subjected to pyrolysis as in the previous experiment. Ether (15 ml) containing pyrogallol was added to the distillate, and the ethereal solution was washed with 10 ml of water, dried with magnesium sulfate, and distilled. The product, amounting to 13.0 g (71%), was 1-cyclopenten-1-yl vinyl ketone; b.p. 63-65° (7 mm); n_D^{20} 1.5078.

Found %: C 78.54; H 8.50. $C_8H_{10}O$. Calculated %: C 78.68; H 8.20.

4-Methyl-1,4-hexadien-3-one (II). From 23.23 g (0.127 mole) of 1-diethylamino-4-methyl-4-hexen-3-one [3] and 12 ml (0.19 mole) of methyl iodide in 20 ml of ether the methiodide was prepared as in the preceding experiment. The pyrolysis was carried out at a bath temperature of up to 200° under a residual pressure of 25-30 mm. The distillate obtained was treated further as indicated above. The product, amounting to 8.9 g (63%), was 4-methyl-1,4-hexadien-3-one (II); b.p. 62-64° (21 mm); n_D^{19} 1.4782.

Found %: C 76.03; H 9.19. $C_7H_{10}O$. Calculated %: C 76.3; H 9.08.

2-Methyl-1,4-pentadien-3-one (I). The methiodide of 5-diethylamino-2-methyl-1-penten-3-one [3] was prepared from 18 g of the amino ketone and 10 ml of methyl iodide in 25 ml of ether and subjected to pyrolysis at a bath temperature of up to 210° under a residual pressure of 75 mm. Treatment of the distillate as indicated above gave 2.0 g (20%) of 2-methyl-1,4-pentadien-3-one (I); b.p. 61-63° (95 mm); n_D^{20} 1.4546. Its dinitrophenylhydrazone melted at 134-135°.

Found %: C 52.22; H 4.36. $C_{12}H_{12}O_4N_4$. Calculated %: C 52.11; H 4.37.

Reaction of 4-Methyl-1,4-hexadien-3-one (II) with Methylamine. With cooling and stirring, 15 ml of 36% aqueous methylamine solution was added gradually to 11.5 g of 4-methyl-1,4-hexadien-3-one. There was a vigorous reaction with evolution of heat. The base was isolated from the resulting homogeneous solution by saturation with potassium carbonate and extraction with ether. The ether extracts were dried with potassium carbonate and distilled. The product, amounting to 10.5 g, was 1,2,3-trimethyl-4-piperidone; b.p. 65-67° (7 mm); $n_D^{19.5}$ 1.4700. The base was freed from imine impurity by dissolving it in 5 N HCl and heating the solution at 95° for 30 minutes. After redistillation the piperidone had b.p. 63-64° (2.5 mm) and n_D^{20} 1.4678.

Found %: C 68.33; H 10.73; N 10.37. $C_8H_{15}NO$. Calculated %: C 68.30; H 10.62; N 9.93.

Its picrate melted at 172° from alcohol.

Hydrogenation of 1-Cyclopenten-1-yl Vinyl Ketone (IV). 1-Cyclopenten-1-yl vinyl ketone (IV) (12.5 g) was hydrogenated over palladium deposited on calcium carbonate, first in dioxane (absorption of hydrogen ceased before saturation was complete), and then in methanol. The catalyst was separated, and the solvent was distilled off. Vacuum distillation of the residue gave 11.5 g of cyclopentyl ethyl ketone; b.p. 49-50° (6 mm); n_D^{17} 1.4467; semicarbazone m.p. 133-134° (Mousseron gives 133-134° [8]).

SUMMARY

A new convenient method was developed for the synthesis of alkenyl vinyl ketones: the pyrolysis of methiodides of alkenyl 2-dialkylaminoethyl ketones prepared from hydrocarbons derived from 1-buten-3-yne. The alkenyl vinyl ketones (divinyl ketones) described form convenient starting materials for the preparation of 4-piperidones, which are of great interest for the synthesis of highly active analgetics.

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LITERATURE CITED

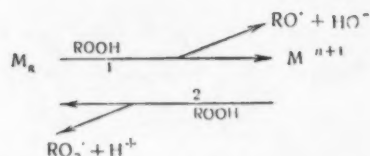
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*Original Russian pagination. See C. B. Translation.

Initiation of polymerization at low temperatures is associated only with Reaction (1). The role of the dienol consists only in the reduction of ferric or cupric to ferrous or cuprous. This system can be used to initiate the polymerization of monomers in aqueous emulsions under acid and alkaline conditions at temperature ranging down to -50° [3].

Reversible systems containing peroxides or hydroperoxides that are soluble in hydrocarbons, salts of metals of variable valence, and organic reducing agents can be used to initiate the polymerization of monomers in anhydrous hydrocarbon media [4, 5]. The main effect of the absence of water is the retardation of the reduction of M^{n+1} to M^n . In the case of benzoin the reduction of Fe^{3+} to Fe^{2+} proceeds as a bimolecular reaction with an activation energy of 20 kcal/mole. The apparent activation energy for the decomposition of cumene hydroperoxide in presence of benzoin and iron naphthenate is 18 kcal/mole, as against 28 kcal/mole for its thermal decomposition. The closeness of the values found for the activation energy illustrates the determining part played by the reduction of Fe^{3+} to Fe^{2+} in the kinetics of the action of the system as a whole. In this connection, the use of more powerful reducing agents, e.g., diethyl dihydroxymaleate [5], results in increased effectiveness of the system. In absence of monomer and oxygen such reversible systems lead to the cross-linking (vulcanization) of unsaturated polymers (e.g., rubbers), both in solution and in the mass [6].

It is of particular interest to examine systems consisting of hydroperoxides and very small amounts of salts of metals of variable valence in absence of reducing agents. At 40° and above, the naphthenates of Co, Cu, Pd, Mn, Ag, Pb, Cr, Ni, and Fe in hydrocarbon solutions bring about the decomposition of hydroperoxides and the initiation of polymerization [5] and oxidative processes. The activities of the metals in polymerization diminish in the above order from cobalt to iron. Investigation of the mechanism of the reaction showed that in these systems there develops a reversible cycle of alternating oxidation and reduction of the metal compound by the hydroperoxide [7].

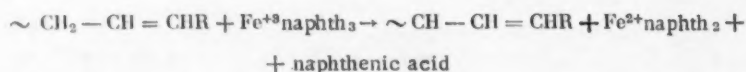


Reaction (2), in which the hydroperoxide plays the part of a reducing agent, leads to the formation of the radical $RO_2\cdot$. When the decomposition is carried out in benzene, in which chain propagation is less probable, reaction probably proceeds by recombination of radicals with formation of oxygen, the yield of which attains 0.35 mole per mole of hydroperoxide [7]. The over-all rate of the process is determined by the kinetics of Reaction (2). It is possible that the mechanism of the decomposition of hydrogen peroxide in presence of salts of metals of variable valence must be regarded in the same way. Owing to the higher reducing power of hydrogen peroxide, its decomposition in presence of metal salts in the higher oxidation state proceeds at lower temperatures.

Systems Containing Salts of Metals of Variable Valence as Oxidizing Agents. The impossibility of utilizing the reduction of Fe^{3+} by dienols for the initiation of polymerization is probably due to the fact that salts of iron and other metals form complex compounds with dienols, and reaction proceeds without the formation of free radicals:



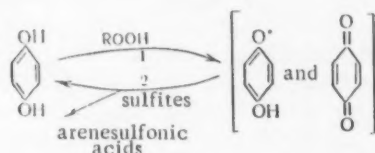
In those cases in which the reducing agent does not form complexes with metal salts, the reaction can be used for the the initiation of free-radical processes; e.g. the reduction of Fe^{3+} and Cr^{3+} by hydrocarbons at 100° can initiate the polymerization of isoprene in a homogeneous medium [8]:



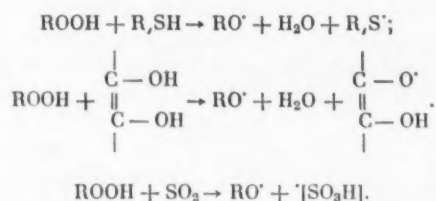
The reduction of ferric naphthenate by an unsaturated polymer chain (rubber) in absence of monomer and oxygen leads to cross-linking of the polymer. This way of forming initial active centers must be taken into account in any appraisal of the part played by salts of metals of variable valence in the development of oxidative processes.

Systems of the Second Type

A system of theoretical and practical interest is one containing hydroquinone, which has been used industrially for the initiation of polymerization in emulsions at $+5^\circ$ [9]. The reaction between a hydroperoxide and hydroquinone cannot be used for the initiation of polymerization because of the inhibiting effect of stable semiquinone radicals that accumulate in the system. These radicals can be removed by the introduction of a third component (sulfites and other compounds) which reduces quinonoid oxidation products to benzenoid compounds. The system acts by the following mechanism:



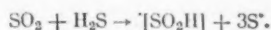
In aqueous alkaline media Reaction (1) proceeds at an appreciable rate even at -15° ; it is accelerated considerably by ammonia, pyridine, or quinoline, which are not changed during the process, but affect the reactivity of the hydroquinone by complex formation [10]. Reaction (2) is almost instantaneous and results in the formation of hydroquinone and sulfonic acids. In this system hydroquinone can be replaced by benzoquinone with the same initiating effect. Various other systems are known in which reaction between oxidizing and reducing agents is accompanied by the formation of two radicals. Reaction of hydroperoxide with a thiol, sulfur dioxide, or other reducing agent leads to the initiation of free-radical polymerization and to the cross-linking of polymers [6]:



A hydroperoxide- SO_2 system brings about rapid cross-linking of unsaturated polymers at low temperature. In styrene the reaction results in the formation of a polysulfone containing sulfo groups. Nitric oxide inhibits this process [11]. Systems of this group, in which SO_2 plays the part of an oxidizing agent, are of considerable interest [12]. As reducing agents hydrogen sulfide, trichlorobenzenethiol and other thiols, and dienols can be used. It is well known that reaction between SO_2 and H_2S results in the vulcanization of rubber at room temperature (Peachy process) [13]. It was previously supposed that the vulcanization effect is associated with the action of active sulfur in the "moment of formation" by the reaction



As in many other oxidation-reduction reactions of this type, the mechanism of the process can be understood correctly only by examination of the intermediate bimolecular stages:

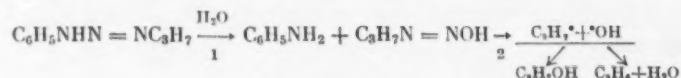


The replacement of hydrogen sulfide by trichlorobenzenethiol, which is similar in reducing properties, results in instantaneous vulcanization of rubber even at 0° , although this process is not accompanied by the separation of elementary sulfur. The reaction is accompanied by the addition of SO_2 and trichlorobenzenethiol to the unsaturated polymer chain. Nitric oxide inhibits this process. It follows that the Peachy process is a special case of the oxidation-reduction initiation of free-radical processes by systems not containing peroxides.

Systems of the Third Type

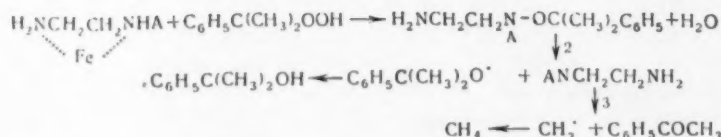
Systems Containing Triazenes. A system containing diazoaminobenzene and activators was the first system used (as early as 1939) for the initiation of emulsion polymerization [14]. In recent years we have studied the

mechanism of the action of systems containing aliphatic-aromatic triazenes. The breakdown of such triazenes in aqueous-emulsion media is again greatly accelerated by the presence of hydroquinone, ascorbic acid, and ferrous and ferric sulfates, and it was shown these latter substances remain unchanged in the course of the breakdown of the triazene [15], even when the triazene is in great excess. Our investigations showed that the mechanism of the action of systems containing triazenes is as follows:

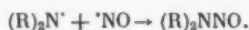


Carbohydrates, hydroquinone, dienols, and other activators catalytically accelerate the addition of water to the triazene (Reaction (1)), and this stage determines the over-all kinetics of the process. Reaction (2) (spontaneous breakdown of the diazo-hydroxide) gives rise to free-radical reactions. Hence, in these systems water is utilized directly in the formation of hydroxyl radicals [15, 16]. In the case of diazoaminobenzene, breakdown of the diazo-hydroxide results in the first place in the formation of the $C_6H_5N=N^{\cdot}$ radical. This was confirmed by the presence of chromophoric groups at the ends of the polystyrene chain; as a result it was possible to use a colorimetric method of determining the molecular weight of the polymer [17].

Systems Containing Ethylenediamine and Polyethylenepolyamines. The use of polyethylenepolyamines in combination with hydroperoxides, for the initiation of polymerization at low temperatures, was first proposed by Whitby and co-workers [18]. On the basis of the view that free radicals are formed by reaction between the hydroperoxide and the amine, it would be expected that there would be a symbatic relationship between the kinetics of the decomposition of a hydroperoxide and the kinetics of polymerization. However, investigation showed that polymerization is initiated at low temperature after complete exhaustion of cumene hydroperoxide [19, 20]. The experimental results indicate the formation of a new intermediate compound of nonperoxide character which can in one way or another initiate the polymerization process. Study of the compositions of the products formed in reactions between cumene hydroperoxide and amines led to the following view concerning the mechanism of the action of the systems:

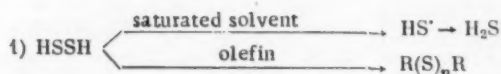


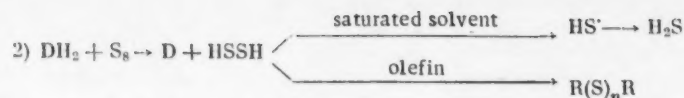
In absence of monomer, reaction of the free radicals with amines and other compounds results in the formation of methane and α, α -dimethylbenzyl alcohol. The significance of Reaction (3) increases greatly with rise of temperature. In presence of monomers, the formation of methane is completely suppressed and the yield of the benzyl alcohol is greatly reduced. The formation of free radicals in which the reaction center is at a nitrogen atom was proved by the formation of nitrosamines when reaction was carried out in presence of nitric oxide [19].



Moreover, it was shown that nitrogen was present in the polymer, which indicates that amine fragments enter the polymer chain [19, 20].

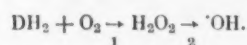
Systems Containing Sulfur and Oxygen as Oxidizing Agents. The reaction of sulfur with various reducing agents (hydroxy aldehydes and ketones, ethanolamines, ethylenediamine and its derivatives) that can act as accelerators in vulcanization with sulfur results at 100–130° in the formation of hydrogen sulfide, the yield of which approaches the theoretical values in certain cases [12]. The use of an olefin, which acts as an acceptor for intermediate reaction products, as the medium for reaction between these reducing agents and sulfur leads to the suppression of the formation of hydrogen sulfide. The main reaction products are the compounds $R(S)_nR$, in which n ranges from 1 to 4. Completely analogous results were obtained in a study of the breakdown of hydrogen disulfide in an olefin medium [21, 22]:





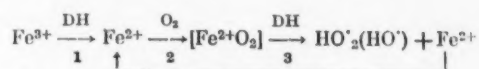
The formation of mono-, di-, and tetra-sulfides is associated with the chain process of breakdown of H_2S_2 , which leads to the generation of the radicals HS^\cdot and HS_2^\cdot . The liberation of hydrogen sulfide was shown to be determined solely by the disproportionation of these radicals.

Another example is provided by systems in which the oxidizing agent is oxygen [23]:

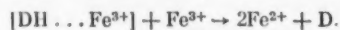


The reducing agents used in these systems may be phenylhydrazine, hydrazobenzene, and other compounds readily oxidized by oxygen in hydrocarbon media with formation of hydrogen peroxide, which serves as an initiator for the oxidation of olefins. The primary oxidation act (Reaction (1)) is probably a simple bimolecular reaction proceeding without the formation of free radicals. Reversible systems that act with the participation of oxygen are specially interesting. These systems contain iron salts soluble in hydrocarbons and reducing agents capable of converting ferric salts into ferrous. As reducing agents in these systems we may use hydroxy carbonyl compounds (benzoin), dienols, alkylhydroquinones, thiols, etc.

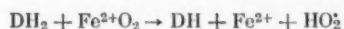
The mechanism by which the systems act is as follows:



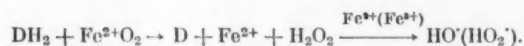
The primary act is undoubtedly reaction between reducing agent and Fe^{3+} , which, as shown for the cases of benzoin and diethyl dihydroxymaleate [6], goes fairly rapidly at 20–50°:



The second stage is the oxidation of ferrous naphthenate, which in ethylbenzene solution proceeds very vigorously even at 0°. The oxidation of ferrous salts is considered to proceed through the intermediate stage of peroxy compounds of iron (FeO) [24] or (FeO_2) [25], which have higher oxidation potentials than ferric iron. These intermediate compounds must react with reducing agents more rapidly than ferric salts do with formation of free radicals:

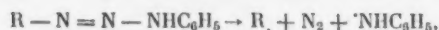


or



Systems of this type are of considerable interest for the initiation of the oxidation of olefins at low temperatures. It is extremely interesting that di-tert-butylhydroquinone, which is commonly used as an inhibitor that protects polymers from the development of chain oxidative and cross-linking processes, begins to assume the function of an activator of these same processes in presence of iron salts that are soluble in the polymers. This phenomenon is more general; this is illustrated by the possibility of using such inhibitors as hydroquinone, benzoquinone, pyrogallol, and copper salts for the effective initiation of free-radical processes. We must point out the similarity of many of the systems studied, in particular systems acting with the participation of oxygen, dienols, and iron salts, to biochemical systems. Oxidation-reduction systems have now found extensive use in technology for the initiation of polymerization at low temperatures; in the future they may become just as important for the initiation of oxidative and other chain processes in hydrocarbon media.

Let us pass to an examination of the main results obtained in our studies of the reactions of free radicals in model systems. For the generation of free alkyl radicals we used aliphatic-aromatic triazenes, which decompose as follows when heated in solution:



with an activation energy which varies among the various triazenes over the range 28-31 kcal/mole [26, 27]. An investigation of the thermal-decomposition products of triazenes in cumene solution enabled us to confirm, on the basis of numerous examples, the correctness of the view that the activity of a free alkyl radical in the elimination of an H atom diminishes with increase in the length of the hydrocarbon chain and in passing from primary free radicals to secondary and tertiary [28-31].

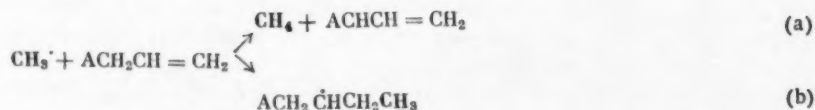
Rupture of C=C Bonds. Investigation of the reactions of various free radicals with unsaturated compounds [21, 22, 32, 33] has enabled us to give a clear picture of the relative reactivities of internal and external double bonds. The conclusions concerning the reactivities of double bonds were based on the investigation of three different reactions (Table 1).

TABLE 1

Rupture of C=C Bonds Under the Influence of Free Radicals

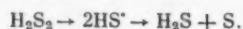
Hydrocarbon	Initiator concentration (moles %)	Temperature (°C)	Yield (%)
Butane	3	110	54
Cumene	1.2	120	56
Cyclohexene	1.2	120	61
2-Butene	3	110	30
1-Heptene	3	110	12
Isobutene	3	110	8
α -Methylstyrene	3	110	0
			H ₂ S
Ethylbenzene	1 mole/liter	70	98
Cyclohexene		50	62
2-Pentene		50	48
1-Pentene		50	9
Styrene		70	5
Isoprene		70	2
			[(CH ₃) ₂ CCN] ₂
Benzene	1.2	80	97
Cumene	1.2	80	82
2-Butene	20	80	79
1-Heptene	20	80	55
α -Methylstyrene	5	80	34

1. In the decomposition of methylphenyltriazenes in an unsaturated hydrocarbon medium two competing reactions occur:



The reduction in the yield of methane, which is a consequence of the addition of $CH_3 \cdot$ radicals to double bonds, characterizes the reactivity of the unsaturated component.

2. As we have shown, the formation of hydrogen sulfide and sulfur in the decomposition of H_2S_2 in a hydrocarbon medium is the result of the disproportionation of $HS \cdot$ radicals:



This view is supported by the fact that the two products are formed in equivalent amounts. The extent to which hydrogen sulfide is formed in the decomposition of H_2S_2 in an unsaturated solvent serves as a criterion of the effectiveness of a given compound as an acceptor of HS^\bullet radicals.

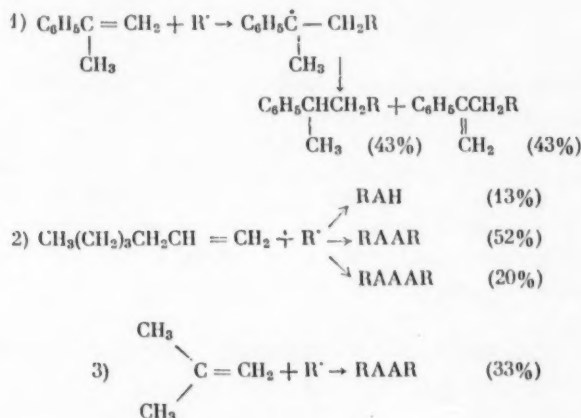
3. The interaction of 1-cyano-1-methylethyl radicals with unsaturated compounds is characterized by the change in the yield of the product of the recombination of these radicals, tetramethylsuccinonitrile. This compound, which is formed by the decomposition of 2,2'-azobis[2-methylpropionitrile] in an inert solvent in almost theoretical yield, is present to a diminishing extent in the decomposition products of this initiator as the extent to which $(\text{CH}_3)_2\text{C}-\text{CN}$ radicals undergo addition at double bonds increases.

The results obtained for all the radicals studied lead to the conclusion that the double bonds of vinyl and isopropenyl groups undergo addition reactions with free radicals much more readily than internal double bonds do. The absence of any tendency for free methyl radicals to add to cyclohexene is probably associated with the enhanced mobility of H atoms of methylene groups in the α -position to a double bond. HS $^{\cdot}$ radicals, which are not capable of reaction with removal of an H atom, add to cyclohexene fairly readily. Our results, and also data in the literature on the reactivity of free alkoxyl radicals, enable us to represent the features peculiar to the various radicals in the reactions with unsaturated compounds by the following scheme:

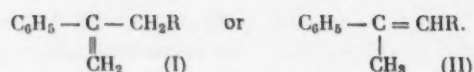


A study of the products of the interaction of free radicals with unsaturated compounds, as carried out in the case of $(\text{CH}_3)_2\text{C}-\text{CN}$ radicals, provides an explanation of the impossibility of obtaining high polymers from α -olefins by the free-radical mechanism. By investigation of the products of the decomposition of 2,2'-azobis[2-methylpropanitrile] in α -methylstyrene, isobutene, and 1-heptene, it was established that the main type of transformations in all cases is termination of reaction by the reaction of RA^\bullet radicals with one another (A = olefin molecule) (see scheme). For 1-heptene and isobutene this reaction results in the formation of recombination products (RAAR), and in the case of α -methylstyrene the RA^\bullet radicals undergo disproportionation with formation of the corresponding saturated and unsaturated compounds (RAH and RB , in which B is formed from A by loss of an H atom).

Products of the reaction of α -olefins with $(\text{CH}_3)_2\text{C}-\text{CN}$ radicals:



The difference in the behavior of RA^{\cdot} radicals in the case of 1-heptane and isobutene, on the one hand, and α -methylstyrene, on the other, is determined by steric hindrance, which excludes the possibility of recombination in the second case. The particularly important part played by the steric factor in this reaction is illustrated by the following facts: in the case of α -methylstyrene the disproportionation of RA^{\cdot} radicals can give one of two unsaturated products:

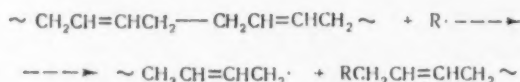


It was shown that the structure of the unsaturated compound corresponds to (I) [32]. Hence, the removal of an H atom in the disproportionation of RA^\cdot radicals occurs at the methyl group, not at the methylene group, in spite of the fact that this requires the rupture of the stronger bond. Hence, in spite of the fact that α -methylstyrene is a fairly active monomer and readily reacts with initial active centers of the free-radical type, in the given case chain growth is impossible because of unfavorable steric conditions. It is for this reason that the formation of high polymers from α -methylstyrene by free-radical polymerization can be effected only by copolymerization with other monomers (e.g. butadiene). As our results show, the inability of other olefins to undergo polymerization by the free-radical mechanism is associated with the low tendency for the monomer to react with its own radicals. In these cases the system is characterized by low activity, both of the monomer and of its radical.

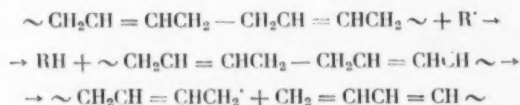
Rupture of C-C and S-S Bonds. As pointed out above, in certain cases various oxidation-reduction systems bring about the degradation of saturated and unsaturated polymers [23]. The same effect is produced also by other sources of free radicals, e.g., peroxides and triazenes [34-36]. Study of the relation of the extent of the degradation to the nature of the initiating radical showed that in their relative activities in this reaction free radicals can be placed in the series:



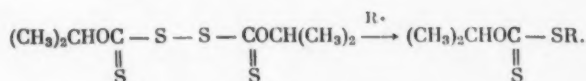
It was suggested at first that the reaction mechanism consists in perpendicular attack of C-C bonds by free radicals:



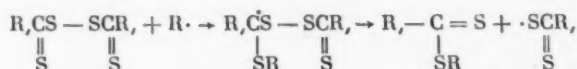
At a conference on reactivity, kinetics, and catalysis Semenov pointed out that a more probably primary act consists in the removal of an H atom with subsequent rupture of a C-C bond in the newly formed free radical. From this point of view the reaction under examination may be represented as follows:



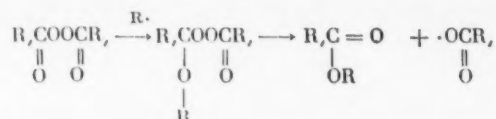
The energetic favorability of the reaction is determined by the formation of a more stable free radical and the appearance of a conjugated system of double bonds at the end of the chain. With such a mechanism the placing of the radicals in the above series of activity becomes understandable. The highest degrading effect is brought about by those radicals which are most active in the removal of H atoms. It is highly significant that $(\text{CH}_3)_3\text{C}^\cdot$ and $(\text{CH}_3)_2\text{C}^\cdot - \text{CN}$ radicals, which do not participate appreciably in acts of removal of H atoms, do not effect the degradation of polymers. The possibility of the rupture of the S-S bond under the action of free radicals was established in a study of the interaction of 1-cyano-1-methylethyl radicals with diisopropyl dithiobisthionofornate [37], which proceeds mainly in the following direction:



From the point of view of the ideas expressed above, it is more probable that the primary act in this case is the addition of a free radical to the C=S double bond. The formation of the final reaction product, as in the case of the rupture of a C-C bond considered above, is the result of the breakdown of the unstable free radical formed in the primary act:

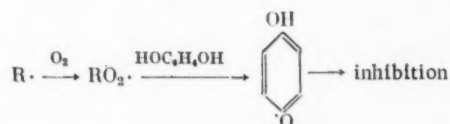


The proposed scheme explains the mechanism of the controlling effect of disulfides in the polymerization process. It is possible that similar acts occur in the chain process of the breakdown of acyl peroxides:

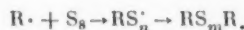


As is well known, the formation of esters in the chain decomposition of peroxides (e.g., the formation of phenyl benzoate from benzoyl peroxide) is indeed observed, though other explanations are usually given. The proposed mechanism must be regarded as highly probable and must be considered together with other possible schemes for the chain decomposition of peroxides.

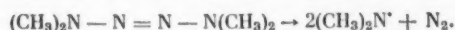
The results which point to specific effects of free radicals of different types are of great interest. In the study of the inhibiting action of polyhydric phenols and secondary aromatic amines on the polymerization process, it was shown that the inhibiting effect appears only in presence of oxygen [38, 39]. Detailed investigation of the kinetics of the process for various systems, and study of reactions in model systems, showed that at temperatures ranging to at least 110° free hydrocarbon radicals do not remove hydrogen atoms from hydroquinone and 2-naphthylamine. The inhibiting effect of polyhydric phenols and aromatic amines in presence of oxygen is probably associated with the formation of RO_2^\cdot radicals, which are highly active in acts of removal of hydrogen and are therefore capable of causing the appearance of semiquinone radicals:



Another example of the specificity of free radicals is the difference in behavior of alkyl and R_2N^\cdot radicals toward sulfur. CH_3^\cdot and other alkyl radicals react almost quantitatively with sulfur with formation of polysulfides [40]:



On the other hand $(\text{CH}_3)_2\text{N}^\cdot$, which is highly active in reactions of H-atom removal and addition to unsaturated bonds [41], does not react at all with sulfur. This radical was prepared by the reaction:



The decomposition of tetramethyltetrazene in cumene, both in absence of sulfur and in its presence, results in the formation of an equal amount of dimethylamine, the product of the removal of an H-atom from cumene by

TABLE 2

Effect of Viscosity on the Yield of Transformation Products of Free Radicals in the Decomposition of 1-Methyl-3-phenyltriazene (concentration of Initiator 10% by weight)

Medium	Yield (%)	
	CH_4	$\text{C}_6\text{H}_5\text{NHCH}_3$
Cumene	49	15
Polystyrene containing 10% of cumene	10	43

$(\text{CH}_3)_2\text{N}^\cdot$ radicals (yield about 90%) [42]. This fact is explained by the low strength of the N-S bond and the impossibility of the existence of the corresponding compounds, at least at elevated temperature. The same conclusion is probably applicable also to RO^\cdot radicals. It is appropriate to mention here that it follows from the low strengths of O-S and N-S bonds that diphenylpicrylhydrazyl, which is often used for the determination of the concentration of free radicals, cannot be regarded as a universal acceptor of free radicals. It follows from these considerations that, at an elevated temperature, its interaction with radicals of the RS^\cdot and RO^\cdot types is improbable.

In conclusion, we wish to point out that the study

of the reactions of free radicals in model systems has enabled us to make an approach to the problem of the relation between primary recombination (the cage effect) and the thermostability of polymers. In an investigation of the products of the thermal decomposition of 1-methyl-3-phenyltriazene in the system polystyrene-cumene, we showed that the viscosity of the medium has a considerable effect on the reaction of primary recombination [43]. The main products of the decomposition of methylphenyltriazene are methane and N-methylaniline, and the formation of the latter is probably due to the recombination of radicals formed in a "cage." It was shown that with increase in the viscosity of the medium the yield of N-methylaniline increases greatly, and there is a simultaneous reduction in the yield of methane (Table 2).

It seems likely that the high thermal stability of polymers of high softening point is to be explained by just such an effect of the viscosity of the medium on the elementary reactions of free radicals. Thus, poly-p-xylylene is stable up to 400°. Decomposition of the polymer starts as soon as it melts. In solution this polymer decomposes already at 302° [44]. There are also other polymers that melt at about 400° and decompose only when they have passed into the molten state. It is probable that in all these cases we are concerned with "superheated" polymers, which start to undergo degradative decomposition only after passage through the glass point, at which temperature the viscosity of the system falls sharply. We may suppose that in rigid systems (below the glass point) the primary thermal acts of C-C rupture do not bring about a chain depolymerization process because of the "cage effect," which results in the return of the system to its original state. Only passage into the elastic region will create conditions for the development of a degradation process, which will be manifested by a sharp fall in the thermal stability of the polymers above their softening points. In this view the stability of polymers in solution should be still lower. These ideas concerning the high thermostability of certain polymers require direct experimental confirmation.

SUMMARY

1. The main types of oxidation-reduction systems for the initiation of free-radical processes in aqueous and hydrocarbon media are examined. The systems are classified according to the mechanisms by which they act.
2. An examination is made of the reactions of free alkyls and heteroradicals with various monomers and polymers occurring with rupture of C-H, C=C, C-C, and S-S bonds.
3. The part played by the "cage effect" in determining the thermostability of polymers is examined.

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HETEROCHAIN POLYESTERS

COMMUNICATION 9. POLYESTERIFICATION CATALYSTS

V. V. Korshak, V. A. Zamiatina, and N. I. Bekasova

The polycondensation of ethylene glycol with terephthalic esters is very slow and is greatly accelerated in presence of catalysts. The rate of reaction and the molecular weight of the polyethylene terephthalate formed are greatly dependent on the nature and amount of the catalyst, and we therefore investigated the action of several catalysts on this process.

TABLE 1

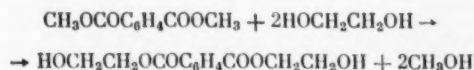
Experiment No.	Catalyst		Duration of heating (hours)		Properties of polyester	
	Composition	Amt. (% by weight)	in stream of nitrogen at 170-275°	in vacuum at 275°	Specific viscosity	Color
1	LiOH·H ₂ O	0,1	6	7	0,26	White
2	LiOH·H ₂ O	0,15	6	7	0,40	"
3	KOH	0,15	6	7	0,21	"
4	KOH	0,20	6	7	0,32	"
5	NaOH	0,05	6	7	0,35	"
6	NaOH	0,075	6	7	0,33	"
7	NaOH	0,10	6	7	0,40	"
8	NaOH	0,15	6	7	0,40	"
9	NaOH	0,20	6	7	0,32	"
10	LiOH·H ₂ O	0,10	8	7	0,49	"
	Al ₂ O ₃	0,05				
11	LiOH·H ₂ O	0,15	8	7	0,52	"
	Al ₂ O ₃	0,05				
12	LiOH·H ₂ O	0,20	8	7	0,57	"
	Al ₂ O ₃	0,07				

Patents on the preparation of polyethylene terephthalate from dimethyl terephthalate and ethylene glycol propose the use of the following as catalysts: alkali metals and their alkoxides and hydroxides [1-3], lead oxide [4], germanium [5], antimony [6], and a mixture of lead oxide, antimony oxide, and triphenyl phosphite [7].

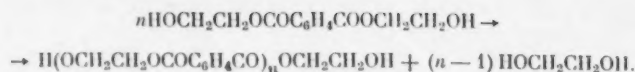
The polymer can be prepared from a mixture of dimethyl terephthalate and ethylene glycol or from bis-2-hydroxyethyl terephthalate, which can be prepared by a method developed by the authors [8]. When dimethyl terephthalate is used, it is first transesterified with ethylene glycol into bis-2-hydroxyethyl terephthalate, which then undergoes polycondensation.

The polycondensation process therefore proceeds in two stages:

First stage: transesterification:



Second stage: polycondensation:



When bis-2-hydroxyethyl terephthalate is used the process beings at the second, polycondensation stage. The use of bis-2-hydroxyethyl terephthalate for the preparation of the polyester has not been described in the literature and was first proposed by one of us and Golubev [9].

TABLE 2

Expt. No.	Catalyst		Properties of polyester	
	Composition	Amount (%) by weight)	Specific viscosity	Color
1	SeO ₂	0,1	0,17	White
2	LiF	0,1	0,18	"
3	SbO	0,1	0,20	"
4	PbO	0,1	0,22	Grayish
5	GeO ₂	0,1	0,23	White
6	GeO ₂	0,2	0,38	"
7	GeO ₂	0,3	0,41	Transparent
8	GeO ₂	0,4	0,30	Yellowish
9	GeO ₂ + LiOH·H ₂ O	0,1 + 0,2	0,27	White
10	GeO ₂ + LiOH·H ₂ O	0,2 + 0,2	0,41	Transparent
11	GeO ₂ + LiOH·H ₂ O	0,3 + 0,2	0,32	Yellow
12	UO ₃	0,05	0,20	White
13	UO ₃	0,10	0,25	"
14	UO ₃	0,15	0,25	Gray
15	UO ₃	0,20	0,23	"
16	UO ₃ + LiOH·H ₂ O	0,1 + 0,2	0,25	White
17	UO ₃ + LiOH·H ₂ O	0,15 + 0,2	0,31	Gray
18	UO ₃ + LiOH·H ₂ O	0,2 + 0,2	0,34	"
19	Al ₂ O ₃ + LiOH·H ₂ O	0,1 + 0,2	0,28	White
20	Without catalyst	—	0,14	"

Our method of investigation was as follows: the experiments were carried out in a test tube having a side tube. The test tube was closed with a rubber stopper carrying a glass tube for the passage of nitrogen. This tube

TABLE 3

Experiment No.	Amt. of bis-2-hydroxyethyl terephthalate taken (g)	Catalyst		Duration of heating (hours)		Properties of polyesters	
		Composition	Amount (% by weight)	In stream of nitro- gen at 170-275°	In vacuum at 275°	Specific viscosity	Color
1	350	GeO ₂	0,2	7	6	0,42	White
2	350	LiOH·H ₂ O	0,2	8	7	0,45	Gray
3	350	PbO	0,02	8	7	0,47	Yellowish
4	350	PbO	0,005	9	7	0,28	White
5	350	Al ₂ O ₃	0,07	7	6	0,49	"
6	365	LiOH·H ₂ O	0,2	7	7	0,50	"
7	350	Al ₂ O ₃	0,07	9	6	0,48	"
8	350	LiOH·H ₂ O	0,17	6	11	0,42	"
9	360	NaOH	0,1	7	15	0,41	"
10	350	NaOH	0,2	8	15	0,43	"
11	350	Without catalyst	—	7	15	0,37	"

passed to the bottom of the test tube so that the nitrogen passed through the reaction mixture. A mixture of 10-15 g of dimethyl terephthalate, the same amount of ethylene glycol (3 moles per mole of ester), and the catalyst was prepared in the test tube, nitrogen was passed, and the mixture was heated in a bath of Wood's metal. The temperature was regulated automatically. The transesterification was carried out at 170° and was completed by raising the temperature slowly to 275° and maintaining this temperature for one hour. The methanol liberated and the excess of ethylene glycol were distilled off into a receiver. The second, polyesterification stage was carried out in a vacuum at 275° (residual pressure 2-3 mm). In the first stage nitrogen was passed at a rate of 1-1.5 liters/hour, and in the second stage it was passed at such a rate that the residual pressure did not rise by more than 0.5 mm. In the polycondensation of bis-2-hydroxyethyl terephthalate the temperature conditions were somewhat different: heating in a stream of nitrogen at 240-275° for three hours and heating in a vacuum at 275° for four hours.

In addition to some of the catalysts indicated above we used also a mixed catalyst of lithium hydroxide and alumina, the active principle of which was probably lithium aluminate, Li_3AlO_3 and LiAlO_2 .

The results of investigations carried out with dimethyl terephthalate are given in Table 1, in which the polyesters obtained are characterized by specific viscosity as 0.5% solutions in cresol.

With lithium, potassium, and sodium hydroxides as catalysts it was possible to obtain polyesters of about the same molecular weight. With the mixed catalyst of lithium hydroxide and alumina, however, a polyester of appreciably higher specific viscosity was obtained. We must point out the slight retarding effect of alumina on the first transesterification stage of the process. Alumina alone is not a catalyst for the first stage of the reaction.

The results of experiments on the polycondensation of bis-2-hydroxyethyl terephthalate are given in Table 2.

On the average, the polyesters obtained in this series of experiments had somewhat lower specific viscosities than those in Table 1, but this is to be explained by the fact that in this series polycondensation in a vacuum was carried out for only four hours.

In many experiments colored or transparent (i.e., not crystallized during slow cooling) polyesters were obtained. This is to be explained by the occurrence of side reactions, the extent of which increases with increase in the amount of catalyst. Of those experiments in which a normal white polyester was obtained, No. 6 and 19 gave the best results: in the first of these a polyester of specific viscosity 0.38 was obtained in presence of 0.2% of germanium oxide, and in the second a polyester of specific viscosity 0.28 in presence of alumina and lithium hydroxide. In absence of catalyst polycondensation was slow, as can be seen from Experiment 20.

The action of some of the more satisfactory catalysts was checked in large-scale experiments in a 1.5-liter steel apparatus provided with a mechanical stirrer. The results are given in Table 3. They show that caustic alkalis can be used successfully as polyesterification catalysts, though the time of heating in a vacuum is then prolonged. Lead oxide is not a very suitable catalyst because it causes discoloration of the polyester. Germanium dioxide, both alone and in combination with lithium hydroxide gives good results, though no better than those given by alumina in combination with lithium hydroxide, which appears to be the best catalyst for the reaction investigated [10].

SUMMARY

The catalytic effects of some oxides and hydroxides in the preparation of polyethylene terephthalate were investigated.

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HETEROCHAIN POLYESTERS

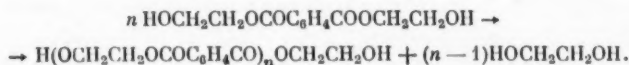
COMMUNICATION 10. KINETICS OF THE POLYCONDENSATION OF BIS-2-HYDROXYETHYL TEREPHTHALATE

V. V. Korshak, N. I. Bekasova, and V. A. Zamiatina

Work on the kinetics of the polycondensation of glycols with dicarboxylic acids can be traced back to that of Menshutkin [1], who already at the close of the last century had investigated the kinetics of reaction between ethylene glycol and succinic acid. The same reaction was studied by Tilicheev [2]. In 1936 Dostal and Raff [3] investigated the kinetics of the polycondensation of succinic acid with ethylene glycol and with 1,4-butanediol in presence and absence of solvent. The polycondensation of phthalic anhydride with various glycols has been studied by many authors [4-7].

Flory [8] investigated several cases of the kinetics of the polyesterification of dicarboxylic acids with glycols and found that in presence of p-toluenesulfonic acid the process has a bimolecular mechanism, whereas in absence of catalyst it behaves as a third-order reaction. Several later investigations confirmed these conclusions [9-11]. However, Davies [12], who investigated the polyesterification of sebacic acid with diethylene glycol, established that this reaction is essentially (to the extent of 80%) of second order. Rafikov and Korshak [13] studied the kinetics of the polyesterification of adipic acid with ethylene glycol and with 1,10-decanediol. They found that, in the investigated temperature range, the reaction proceeds by a bimolecular mechanism and the rate constants vary with temperature in accordance with the Arrhenius equation. Korshak and Vinogradova [14] investigated the kinetics of the polyesterification of sebacic acid with 1,6-hexanediol and also the polycondensation of bis-2-hydroxyethyl sebacate in presence of catalysts [15].

The polycondensation of bis-2-hydroxyethyl terephthalate, which is of considerable interest in that it results in the formation of polyethylene terephthalate, has received no attention in the literature. In this paper we present results of kinetic investigations on this reaction, which proceeds according to the following equation:



EXPERIMENTAL

The polycondensation was carried out in a 200 ml two-necked round-bottomed flask. The main neck of the flask was closed with a rubber stopper through which passed the orienting tube of a mechanical stirrer fitted with a stuffing box and also two glass tubes, one for the introduction of nitrogen and the other for the exit of nitrogen and ethylene glycol vapor. Ethylene glycol was collected in a graduated receiver. The side neck of the flask carried a thermometer immersed in the reaction mixture; this neck was used also for the removal of test samples. Purified dry nitrogen was passed over the reaction mixture at 0.25 liter/hour. The flask was heated in a metal bath, the temperature of which was regulated automatically with the aid of a contact thermometer and a relay. The temperature was constant within $\pm 1^\circ$ in the bath and within $\pm 0.5^\circ$ in the flask. The flask was charged with bis-2-hydroxyethyl terephthalate and lowered into the bath, which had been heated previously to the required temperature; the ester rapidly melted and the stirrer was switched on. The start of the reaction was taken to be the time at which the flask was immersed in the bath, since it was observed that reaction then set in very quickly.

In all the experiments 120 g of bis-2-hydroxyethyl terephthalate (m.p. 112°) was introduced into the flask and, if necessary, catalyst was added. At definite intervals of time the amount of ethylene glycol liberated was noted and a sample of the polycondensate was taken simultaneously, with the aid of a glass rod. The amount of ethylene glycol distilled off was measured in milliliters and then expressed in grams, and a correction was made

TABLE 1

(242°, catalyst LiOH and Al₂O₃)

Expt. No.	Time (min.)	Amount of ethylene glycol (g)	M from acetyl value	P from ethylene glycol formed, %	P from acetyl value (%)	K from ethylene glycol formed	K from acetyl value
1	20	6,87	330	23,46	23,04	0,003893	0,003892
	40	10,77	420	36,77	39,52	0,003693	0,004149
	70	13,35	480	45,59	47,08	0,003036	0,003228
	100	17,20	650	58,73	60,92	0,003615	0,003966
	160	20,08	870	68,55	70,80	0,003460	0,003849
	280	23,02	1110	78,57	77,11	0,003326	0,003056
	400	24,69	1550	84,31	83,62	0,003412	0,003242
	580	25,45	2446	86,24	89,61	0,002745*	0,003776
2	K _{mean}					0,003397	0,003633
	20	6,99	320	23,85	20,62	0,003978	0,003299
	40	10,87	425	37,11	40,22	0,003747	0,004272
	70	13,42	473	45,82	46,31	0,003069	0,003124
	100	17,74	644	60,57	60,55	0,003903	0,003898
	160	20,20	814	68,97	68,80	0,003528	0,003501
	280	22,20	1290	75,79	80,31	0,002840	0,003699
	400	24,91	1600	85,05	94,12	0,003612	0,003364
K _{mean}						0,003525	0,003594

* Value not taken into account in the calculation of K_{mean}.

for the amount of ethylene glycol that could have been liberated from the test sample at a later stage. The test samples contained a considerable amount of ethylene glycol which had already been liberated but had not yet succeeded in escaping from the reaction mixture; they were therefore dried to constant weight at 110° in a vacuum in an Abderhalden apparatus. Hydroxyl contents were then determined, and, in the case of the samples of higher molecular weight, specific viscosity measurements were made.

TABLE 2

Expt. No.	Reaction temperature (°C)	Catalyst	K _{mean} from acetyl value
1	242	—	0,001108
2	242	—	0,001196
1	242	LiOH · H ₂ O	0,002894
2	242	LiOH · H ₂ O	0,002860
1	242	LiOH · H ₂ O and Al ₂ O ₃	0,003633
2	242	LiOH · H ₂ O and Al ₂ O ₃	0,003594
1	251	—	0,002128
2	251	—	0,002120
1	264	—	0,004353
2	264	—	0,004334
1	275	—	0,008476
2	275	—	0,008965
1	275	LiOH · H ₂ O and Al ₂ O ₃	0,027420
2	275	LiOH · H ₂ O and Al ₂ O ₃	0,025020
1	285	—	0,015080
2	285	—	0,015530

The determination of hydroxy groups was carried out by acetylation in accordance with the method of Verley and Bolsing, as modified by Kiselev [16] specially for the investigation of macromolecular compounds. A

TABLE 3

Temperature range (°C)	Activation energy (cal/ mole)
251—242	34280
264—251	33720
275—264	35630
285—275	38280
264—242	32360
285—242	35110
275—251	34180
285—251	35210
275—242	34210
285—264	36690
Mean	34980 ± 3000

From the amount of ethylene glycol liberated and the acetyl value the progress of reaction was calculated; for this purpose Equations (1) and (2) were used.

$$P = \frac{A}{29.29}, \quad (1)$$

in which A is the amount (g) of ethylene glycol liberated up to the moment at which the sample is taken, and 29.29 is the theoretically calculated amount of ethylene glycol which would be liberated from 120 g of bis-2-hydroxyethyl terephthalate on completion of reaction.

$$P = \frac{39.37 - \frac{10000}{M}}{39.37}, \quad (2)$$

in which 39.37 is the acetyl value of bis-2-hydroxyethyl terephthalate expressed as milliliters of 0.2 N NaOH per gram, and M is the molecular weight of the sample as determined from hydroxyl content.

The reaction rate constants were calculated from the equation for reactions of the second order [17]:

$$K = \frac{P}{(1 - P) c_0 t},$$

in which c_0 is the initial concentration (mmoles/g) of active groups. In our case

$$c_0 = \frac{1000}{254} = 3.937 \text{ mmoles/g}$$

(P is the progress of reaction at the time of sampling, and t is the time (minutes) from the start of reaction).

Activation energies were calculated from the Arrhenius equation [18]:

$$A = 4.57 \frac{\lg \frac{K_1}{K_2}}{\frac{1}{T_2} - \frac{1}{T_1}}.$$

We studied the kinetics of the process at 242°, 251°, 264°, 275°, and 285° in absence of catalyst, at 242° and 275° in presence of a catalyst consisting of 0.2% by weight of lithium hydroxide and 0.1% by weight of alumina, and also at 242° in presence of 0.2% of lithium hydroxide alone. All experiments were carried out in duplicate; the agreement was quite satisfactory.

sample weighing 0.2-0.8 g was refluxed for 90 min. with 2-4 ml of a mixture of 1 part acetic anhydride and 3 parts pyridine. Samples of polyesters having a molecular weight of more than 1500 were heated for not less than 3.5 hours, as otherwise acetylation was not complete. When cool, the contents of the flask were diluted with 5 ml of water and titrated with 0.2 N NaOH to phenolphthalein. A control experiment was carried out.

The molecular weight was calculated from the equation

$$M = \frac{10000a}{b}$$

in which a is the weight of polyester (g) and b is the amount of 0.2 N NaOH required in the titration (ml).

By way of example we give the results on the kinetics of polyesterification at 242° in presence of lithium aluminate in Table 1. Analogous results were obtained in the other experiments; they are given in Table 2 and represented graphically in Figures 1 and 2.

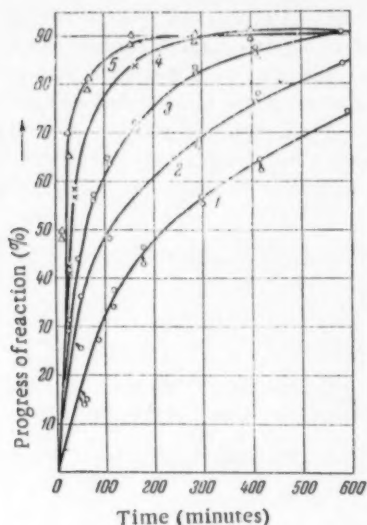


Fig. 1. Kinetics of the polycondensation of bis-2-hydroxyethyl terephthalate without catalyst at a temperature of 1) 242°, 2) 251°, 3) 264°, 4) 275°, 5) 285°.

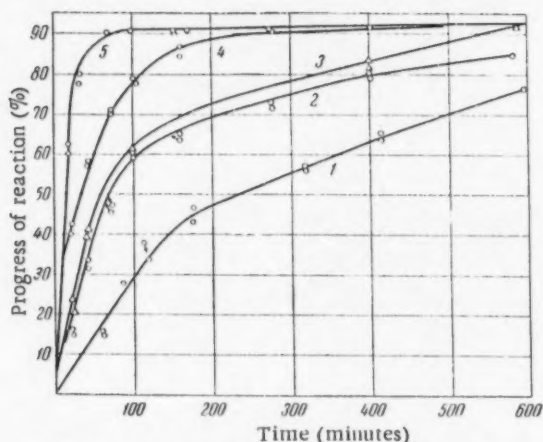


Fig. 2. Kinetics of the polycondensation of bis-2-hydroxyethyl terephthalate in presence and absence of catalysts: 1) 242° without catalyst; 2) 242°, catalyst $\text{LiOH} \cdot \text{H}_2\text{O}$; 3) 242°, catalyst $\text{LiOH} \cdot \text{H}_2\text{O} + \text{Al}_2\text{O}_3$; 4) 275° without catalyst; 5) 275°, catalyst $\text{LiOH} \cdot \text{H}_2\text{O} + \text{Al}_2\text{O}_3$.

From the rate constants we calculated activation energies; the values obtained for various temperature ranges are given in Table 3.

Fig. 3 shows the relation of rate constant to temperature; it is in accord with the Arrhenius equation.

DISCUSSION OF RESULTS

In all the experiments, and particularly in those carried out at high temperatures, the progress of reaction calculated from the amount of ethylene glycol liberated is considerably lower than that calculated on the basis of the determination of hydroxy groups. This is explained by the fact that not all of the ethylene glycol liberated in the reaction passes into the receiver; part of it remains in the liquid and vapor phases in the flask, part of it vaporizes during the taking of samples, and some of it is carried away by the nitrogen. It is quite obvious that, with rise in temperature, these losses of ethylene glycol will increase. Hence, a more correct characterization of the kinetics of the reaction is given by the rate constants calculated from hydroxyl contents, rather than from amounts of ethylene glycol liberated. In the experiments carried out at 264°, 275°, and 285° the rate constants were therefore calculated only from hydroxyl contents. In each separate experiment there were small variations in the values of rate constants* calculated from hydroxyl contents, but there was close agreement between mean values. With rise in temperature the rate constants increase in a regular manner.

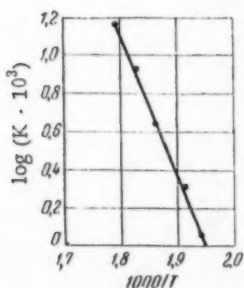


Fig. 3. Relation of polyesterification rate constant to temperature.

As will be seen from Fig. 1, at high temperatures (275° and 285°) the polycondensation attains an equilibrium

state (progress of reaction of 90-91%) fairly quickly. Further heating does not result in appreciable further increase in molecular weight. Catalysts increase the rate of polycondensation by a factor of 2-3; a particularly good result is obtained by the use of lithium aluminate, prepared from lithium hydroxide and alumina.

The close agreement between values of activation energy calculated for different temperature ranges enables us to conclude that the polyesterification of bis-2-hydroxyethyl terephthalate follows a second-order equation.

SUMMARY

1. A study was made of the polyesterification of bis-2-hydroxyethyl terephthalate at atmospheric pressure in the temperature range 240-285°, and the rate constants of the reaction were determined.
2. The activation energy was calculated and found to be 35,000 cal/mole.
3. It was shown that the polyesterification of bis-2-hydroxyethyl terephthalate in absence of catalyst proceeds in accordance with the laws of a second-order reaction.
4. It was noted that after 6-7 hours at 275° or after 3 hours at 285° an equilibrium is established and further heating has scarcely any effect on the molecular weight of the polyester.
5. A study was made of the polyesterification of bis-2-hydroxyethyl terephthalate in presence of catalysts lithium hydroxide and alumina. Catalysts increase the rate of reaction by a factor of 2-3.
6. It was shown that polycondensation in presence of catalysts proceeds in accordance with second-order laws.

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SYNTHESIS OF POLYALKYNEARYLS

COMMUNICATION 4. EFFECT OF TEMPERATURE ON THE COURSE OF THE COPOLYCONDENSATION OF BENZENE AND CHLOROBENZENE WITH 1,2-DICHLOROETHANE

G. S. Kolesnikov, V. V. Korshak, and A. P. Suprun

Copolycondensation reactions have recently been studied by many workers, mainly in relation to the synthesis of mixed polyamides and polyesters. We may refer, for example, to the work of one of the present authors in collaboration with Frunze [1, 2], and the work of Evans and co-workers [3], of Izard [4], and of Edgar and co-workers [5, 6]. Until now study has been concerned mainly with the effect of the composition of the mixture of reactants on the properties of the polycondensation product formed, and it has been assumed that the compositions of the copolymer and the original mixture of reactants (with respect to the contents of residues that remain unchanged during the reaction) are identical. This assumption is in general true only when polycondensation equilibrium is established; if equilibrium has not been established, it is true only when the reactants of the same type have identical reactivities.

In absence of polycondensation equilibrium and with reactants differing in reactivity, these reactants will be used up at different rates, as in the case of the copolymerization of vinyl compounds. This will then result in the formation of copolymers which vary in composition during the polycondensation process. As far as we are aware, the copolycondensation process has not yet been investigated with the object of determining the variation in the composition of the copolymer as polycondensation proceeds, and we considered it to be desirable to carry out an investigation in this direction.

EXPERIMENTAL

For the investigation of this aspect of copolycondensation we selected the system 1,2-dichloroethane-benzene-chlorobenzene because it gives a halogen-containing copolymer which is readily analyzed; as catalyst we used aluminum chloride. For this system we studied the main laws governing the course of the process, and the subject of the present paper is the effect of temperature on the course of the polycondensation process.

The polycondensation of 1,2-dichloroethane with aromatic compounds was carried out in a flask fitted with a sealed stirrer, reflux condenser, a device for the introduction of catalyst, and another for the taking of test samples by means of which a definite volume of reaction mixture could be drawn from the flask and rapidly transferred to a flask containing dilute hydrochloric acid. The reaction flask was placed in an ultrathermostat in which the temperature was maintained constant within $\pm 0.02^\circ$, the dichloroethane and aromatic hydrocarbons were introduced into the flask and, when the required temperature had been reached, a weighed amount of catalyst was introduced rapidly.

Polycondensation was allowed to proceed for 3.5 hours, and 22.5-ml samples of the reaction mixture were taken every 30 minutes. The samples were transferred to dilute hydrochloric acid so that reaction was stopped; benzene was added, and the mixture was washed five times with distilled water and dried with calcium chloride. The dried benzene solution was poured off, the calcium chloride was washed with dry benzene, and the washings were added to the main solution. This was then filtered, and benzene, chlorobenzene, and dichloroethane were distilled off. Polycondensation products of low molecular weight were extracted from the residue with boiling alcohol, and the undissolved part was heated in a boiling water bath under reduced pressure, first at the water pump for 30 minutes (15-20 mm), and then at a residual pressure of 3-4 mm for one hour. The copolymer isolated

in this way was weighed; its molecular weight was determined viscosimetrically, and its halogen content was determined.

Attempts at determining the molecular weights of the copolymers by the cryoscopic method were unsuccessful; in all cases the values of molecular weight determined by the cryoscopic method in benzene varied in the range 600-800, whereas those determined viscosimetrically varied over a range of which one limit was several times as high as the other. From the halogen content we determined the statistical-mean molecular weight of the repeating unit of the copolymer and calculated the degree of polymerization.

DISCUSSION OF RESULTS

In order to determine the effect of temperature on the course of the polycondensation process in the system dichloroethane-benzene-chlorobenzene, we carried out experiments at 60°, 65°, 70°, and 75° in which all the other conditions were kept constant: the molar ratio benzene : chlorobenzene was 1 : 1, the ratio (mixture of aromatic compounds) : dichloroethane was 1.5 : 1, and the concentration of aluminum chloride was 3 moles per cent on the amount of aromatic compounds. The results of these experiments are presented in Tables 1-4 and Figures 1-3.

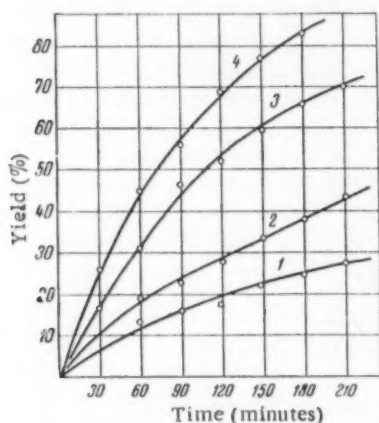


Fig. 1. Relation of yield of copolymer (A) to duration of reaction (t) at 1) 60°, 2) 65°, 3) 70°, 4) 75°.

$A = f_T(t)$ with increase in t . Graphical treatment of the experimental data (Tables 1-4; Fig. 2) showed that $\log \beta$ (the intercept on the axis of ordinates) varies regularly with rise in temperature, whereas μ is almost independent of temperature and has the value 0.71. Taking into account the relationship found, we succeeded in giving an approximate description of the relation $A = f(t, T)$ by means of the equation

$$A = 10^{0.039(T-65.3)} \cdot t^{0.71}$$

Table 5 gives values of the yield of copolymer (A), found experimentally and calculated from the above equation.

It will be seen from Table 5 that the experimentally found and calculated values are in good agreement. The greatest discrepancy between them was observed at 75° for reactions lasting more than 120 minutes. Analogous equations can be deduced for other relative amounts of reacting components.

As will be seen from Tables 1-4, at all temperatures studied with increase in the duration of the polycondensation the chlorine content of the copolymer increases. This is to be explained by the fact that benzene is more active than chlorobenzene in the reaction with dichloroethane, and is therefore more rapidly exhausted from the reaction mixture; as a result, the reaction mixture becomes enriched in chlorobenzene. The lowering of the benzene concentration in the part of the reaction mixture that has not yet reacted naturally results in an increase in the proportion of chlorine-containing residues in the copolymer. From determinations of the chlorine content of the copolymer

From Tables 1-4 and Fig. 1 it will be seen that with rise in temperature the rate of the polycondensation of dichloroethane with the mixture of benzene and chlorobenzene increases. It should be noted that rise in temperature to 70° and 75° results in very vigorous reaction with formation of a cross-linked structure in the late stages of the process. At 70° a three-dimensional polymer is formed after 270 minutes, and at 75° such a polymer is formed after 210 minutes. The relation of yield of copolymer (A) to time (t) at various temperatures (T) with other conditions constant is represented in Fig. 1 by a family of convex curves which, as our investigation showed, can be represented very closely by an equation of the type

$$A = \beta t^\mu$$

or

$$\log A = \log \beta + \mu \log t.$$

In this expression β is the yield of copolymer obtained in 1 minute, and μ expresses the attenuation of the function

TABLE 1

Copolycondensation of Dichloroethane with Benzene and Chlorobenzene at 60°

Duration of reaction (minutes)	Yield of copolymer (%)	Chlorine content of copolymer (%) (mean)	n/m	Basal mole (statistical mean)	Molecular weight of copolymer	Degree of polymerization
60	13,5	1,83	17,3	105,9	1310	12,4
90	16,4	2,05	15,3	106,2	1570	14,8
120	17,9	2,35	13,2	106,4	2080	19,5
150	22,9	2,98	10,1	107,1	1880	17,5
180	25,1	2,70	11,3	106,8	2000	18,7
210	28,3	3,03	9,9	107,2	2140	20,0

TABLE 2

Copolycondensation of Dichloroethane with Benzene and Chlorobenzene at 65°

Duration of reaction (minutes)	Yield of copolymer (%)	Chlorine content of copolymer (%) (mean)	n/m	Basal mole (statistical mean)	Molecular weight of copolymer	Degree of polymerization
30	10,4	2,06	15,2	106,1	1950	18,4
60	18,8	2,21	14,1	106,3	2200	20,7
90	22,6	2,31	13,4	106,5	2380	22,3
120	27,9	2,66	11,5	106,8	2440	22,8
150	33,9	3,12	9,6	107,2	2550	23,8
180	38,7	3,43	8,6	107,6	2630	24,4
210	44,4	3,49	8,4	107,7	2840	26,6

TABLE 3

Copolycondensation of Dichloroethane with Benzene and Chlorobenzene at 70°

Duration of reaction (minutes)	Yield of copolymer (%)	Chlorine content of copolymer (%) (mean)	n/m	Basal mole (statistical mean)	Molecular weight of copolymer	Degree of polymerization
30	16,4	1,77	17,9	105,8	2080	19,6
60	30,9	2,00	15,7	106,1	2150	20,2
90	46,3	2,48	12,4	106,6	2380	22,3
120	51,9	3,30	9,0	107,4	2700	25,5
150	59,4	4,55	6,2	108,8	3140	28,9
180	65,8	5,55	4,8	109,9	3590	32,7
210	69,4	7,17	3,4	111,8	4610	36,5

TABLE 4

Copolycondensation of Dichloroethane with Benzene and Chlorobenzene at 75°

Duration of reaction (minutes)	Yield of copolymer (%)	Chlorine content of copolymer (%) (mean)	n/m	Basal mole (statistical mean)	Molecular weight of copolymer	Degree of polymerization
30	25,8	2,24	13,9	106,3	2160	20,3
60	44,7	2,35	13,2	106,4	2470	23,2
90	55,8	2,89	10,5	107,0	3090	28,9
120	68,1	4,58	6,1	108,8	3990	36,7
150	76,4	5,20	5,2	109,5	5560	50,7
180	82,3	5,36	5,0	109,7	20400	185,5

we may find the relative number of $-\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2-$ and $-\text{C}_6\text{H}_3\text{ClCH}_2\text{CH}_2-$ residues from the equation

$$n/m = \frac{34,05}{\% \text{Cl}} - 1,331,$$

in which \underline{n} is the content of $\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2$ residues in the copolymer, and \underline{m} is the content of $\text{C}_6\text{H}_3\text{ClCH}_2\text{CH}_2$ residues.

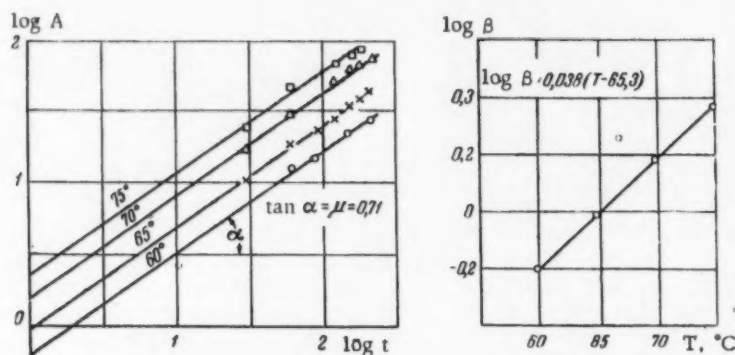


Fig. 2. Graphs for finding $A = f(t, T)$ in an explicit form.

The ratio n/m expresses the number of benzene residues per chlorobenzene residue in the copolymer chain.

TABLE 5

Comparison of Found and Calculated Values of Yields of Copolymer (A)

Reaction temp. (°C)	Duration of reaction (minutes)	Yield of copolymer A (%)		Reaction temp. (°C)	Duration of reaction (minutes)	Yield of copolymer A (%)	
		found	calc.			found	calc.
60	60	13,5	12	70	30	16,4	18
	90	16,4	15		60	30,9	29
	120	17,9	19		120	51,9	48
	150	22,9	22		180	65,8	59
	210	28,3	28		210	69,4	68
65	30	10,4	11	75	30	25,8	26
	60	18,8	18		60	44,7	43
	90	22,6	24		120	68,1	70
	120	27,9	29		150	76,4	82
	150	33,9	34		180	82,3	90
	180	38,7	39				
	210	44,4	43				

If the relative activities of benzene and chlorobenzene toward dichloroethane were equal, then n/m would be equal to the ratio of benzene to chlorobenzene in the original mixture and would not change throughout the polycondensation. However, it will be seen from Tables 1-4 that n/m falls with increase in the duration of reaction. Even in the initial stage of reaction, when the effect of change in the composition of the reaction mixture on the composition of the copolymer is at its least, n/m is not equal to the ratio of benzene to chlorobenzene in the original mixture, which again indicates the differing relative activities of benzene and chlorobenzene in reaction with dichloroethane.

Fig. 3 shows the relation of the content of $-\text{C}_6\text{H}_3\text{ClCH}_2\text{CH}_2-$ residues in the copolymer to the yield of copolymer, and it can be seen that the content of these residues increases in proportion to degree of conversion of the original

compounds into macromolecular compounds and appears to depend very little on the reaction temperature; in other words, the relative activities of the monomers vary very little with change in temperature in the range investigated.

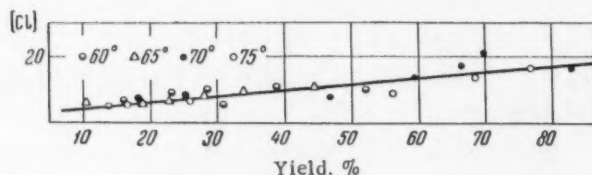


Fig. 3. Relation of content of $-\text{C}_6\text{H}_3\text{ClCH}_2\text{CH}_2-$ residues in the copolymer ([Cl]) to the yield.

Rise in the temperature of the reaction results not only in increase in the yield of copolymer, but also in an increase in the degree of polymerization of the copolymer (Fig. 4). As the chlorine content of the copolymer is not constant, the basal mole is also a variable quantity; the degree of polymerization is therefore a more characteristic quantity than the molecular weight. It will be seen from Tables 1-4 and Fig. 5 that until the yield of copolymer attains 50% the degree of polymerization is close to 20-25 and with increase in yield (up to 50%)

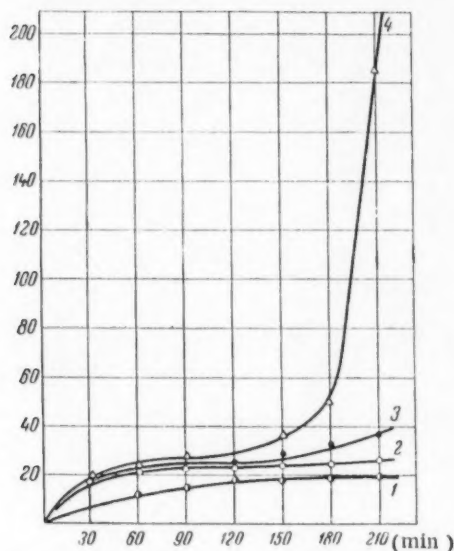


Fig. 4. Relation of the degree of polymerization (p) of the copolymer to the duration of reaction: 1) 60°; 2) 65°; 3) 70°; 4) 75°.

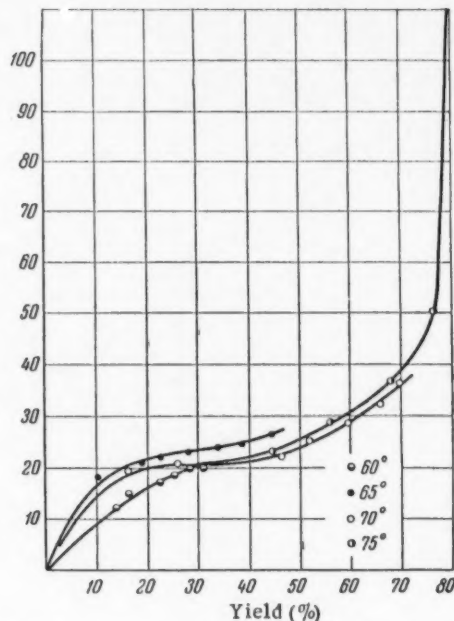


Fig. 5. Relation of the degree of polymerization of the copolymer to the yield.

the degree of polymerization rises only slightly; it is probable that in this period copolymer molecules are formed mainly by reaction between growing polymer molecules and molecules of the original reactants. As the latter become exhausted, growth of copolymer molecules will occur also by the participation of already formed copolymer molecules in the polycondensation reaction in the capacity of aromatic component, so that with a small change in yield the degree of polymerization increases considerably. At 75° increase in yield from 70% to 80% is associated with an almost fivefold increase in the degree of polymerization.

SUMMARY

1. A study was made of the effect of reaction temperature on the course of the copolycondensation of 1,2-dichloroethane with benzene and chlorobenzene in presence of aluminum chloride.

2. It was shown that with increase in the duration of reaction the chlorine content of the copolymer increases, which indicates that the reactivities of benzene and chlorobenzene toward dichloroethane are different.

3. An equation is proposed for the relation of the yield of copolymer to the temperature and duration of reaction for given relative amounts of reactants.

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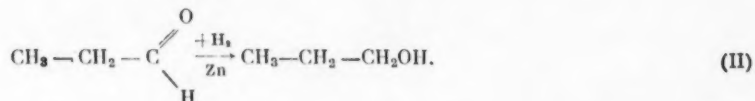
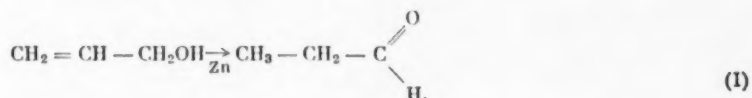
*Original Russian pagination. See C. B. Translation.

BRIEF COMMUNICATIONS

MECHANISM OF THE REDUCTION OF ALLYL ALCOHOL OVER ZINC AND ZINC-COPPER CATALYSTS

L. Kh. Freidlin, M. F. Abidova, and A. S. Sultanov

We showed recently that zinc has high catalytic activity in the reduction of aldehydes and ketones with hydrogen at 50-150° under atmospheric pressure. On the other hand, under these conditions the C=C bond (hexene, cyclohexene) is not hydrogenated. In an investigation of the reduction of allyl alcohol over this catalyst we found unexpectedly that conversion into propyl alcohol begins already at 75°. With rise in temperature propionaldehyde is formed as well as the alcohol. This fact suggested the possibility that in this process hydrogen does not add at the C=C bond, but reduction proceeds by the following mechanism:



In order to verify this suggestion we carried out a series of experiments in which only the isomerization reaction (I) could occur. With this object allyl alcohol was passed over the catalyst in a stream of nitrogen. As was expected, in absence of hydrogen propionaldehyde was formed from allyl alcohol.

We considered it to be of interest to determine how a catalyst containing copper as well as zinc would behave; in presence of copper a terminal C=C bond is generally readily hydrogenated. It was found that, in presence of a catalyst consisting of two parts of copper and only one part of zinc, the reduction of allyl alcohol proceeds by an analogous mechanism.

EXPERIMENTAL

The zinc catalyst was prepared by the leaching of Al-Zn alloy (1 : 1 by weight) with 3% aqueous sodium hydroxide solution at 100° until about 90% of the aluminum (as determined from the volume of hydrogen evolved) had been removed. The zinc-copper catalyst was prepared similarly from an Al-Zn-Cu alloy (50 : 17 : 33 by weight). The leached catalyst was washed until neutral to phenolphthalein, and was introduced in the moist state into the glass reaction tube, which was placed vertically in an electric furnace. The temperature was maintained constant within $\pm 1-2^\circ$ and was measured by means of a thermocouple, the end of which was in the catalyst layer.

Allyl alcohol, b.p. 95.2° (740 mm) and n_D^{20} 1.4115, was passed over the catalyst at a uniform rate with the aid of a doser operated by a clockwork mechanism [1]. In the course of each 40-minute experiment, 8.5 g of allyl alcohol was passed over 125 ml of catalyst (length of layer 14-16 cm). The catalyzate was analyzed for content of aldehyde groups by the oxime method and for C=C groups by the consumption of hydrogen in the hydrogenation of a weighed sample in 96% ethanol in presence of Raney nickel at 20°. It was shown by special experiments that

under these conditions no appreciable hydrogenation of propionaldehyde occurs. The amount of propionaldehyde formed was calculated from the carbonyl value, the amount of unchanged allyl alcohol from the hydrogen value, and the amount of propyl alcohol formed from the difference. The propionaldehyde isolated by fractionation had b.p. 49° (736 mm) and n_D^{20} 1.3658; its 2,4-dinitrophenylhydrazone had m.p. 154° (from ethanol). The residue after the distillation of the aldehyde had b.p. 90-97°; it was treated with bromine in benzene solution with cooling. Distillation of the mixture obtained gave propyl alcohol, b.p. 95-97° and n_D^{20} 1.3840.

TABLE 1

Temperature (°C)	Amount found (% by weight)		Amount found (% by weight)	
	Propionaldehyde	Allyl alcohol	Propionaldehyde	Allyl alcohol
	Zinc catalyst		Zinc-copper catalyst	
75	0.6	92.0	4.4	90.0
87	13.7	78.5	28.3	66.0
100	21.0	71.6	62.3	29.4
125	30.6	63.5	75.4	16.5
150	56.5	38.8		
175	63.5	31.8		

The reaction was smooth, and side reactions were absent. This was confirmed by the fractionation results, and also by the fact that the extent of conversion of the alcohol, calculated on the amount that reacted,* was close to the theoretical value. The results of experiments carried out in a stream of nitrogen are given in Table 1, from which it can be seen that with rise in temperature the extent of the isomerization of allyl alcohol into propionaldehyde increases and attains 63.5% at 175°. The zinc-copper catalyst is still more active in this reaction, and in its

TABLE 2

Tempera- ture (°C)	Amount found (% by weight)		Degree of conversion into propyl alcohol (%)	Amount found (% by weight)		Degree of conversion into propyl alcohol (%)
	Propionalde- hyde	Allyl alcohol		Propionalde- hyde	Allyl alcohol	
	Zinc catalyst			Zinc-copper catalyst		
75	0	87.0	4.6	0	89.5	6.9
87	1.2	78.8	13.8	0	86.0	10.5
100	2.4	73.0	19.5	28.2	22.3	46.0
125	16.4	44.7	34.5	14.1	16.5	65.6
150	22.4	18.7	55.0	5.9	4.7	84.0
175	22.4	17.7	56.3			

presence the yield of propionaldehyde attains 75.4% already at 125°. According to Paul [2], over Raney nickel allyl alcohol is isomerized at 92-95°. The results of experiments on the reduction of allyl alcohol are given in Table 2. In all experiments we took a fourfold excess of hydrogen. It will be seen from a comparison of Tables 1 and 2 that both reactions (isomerization into aldehyde and reduction of the latter to the alcohol) proceed in the same temperature range. In experiments at 75° no aldehyde was detected, but the amount of allyl alcohol converted into propyl alcohol was 4.6%. It is probable that at this temperature the isomerization reaction (I) is only beginning and the aldehyde formed in small amount is reduced to propyl alcohol. On the other hand, in the temperature range 87-175° the isomerization reaction is clearly outstripping the reduction and, in spite of the presence of an excess of hydrogen, part of the aldehyde is not hydrogenated. Comparison of the data in Table 2 shows that the zinc-copper catalyst is more active than the zinc catalyst also in the reduction of the propionaldehyde formed.

* In the tables it is given as percent of the amount passed.

SUMMARY

1. It was shown that zinc and zinc-copper catalysts are highly active in the reduction of allyl alcohol to propyl alcohol at 75-150° in presence of hydrogen at atmospheric pressure.
2. It was found that the reaction proceeds through the intermediate stage of isomerization of allyl alcohol into propionaldehyde. It was shown that the isomerization stage outstrips the reduction stage.
3. In both reactions the zinc-copper catalyst is more active than the zinc catalyst.

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PREPARATION OF CRYSTALLINE POLYPROPYLENE BY THE POLYMERIZATION
OF TECHNICAL PROPENE IN PRESENCE OF TRIISOBUTYLALUMINUM
AND TITANIUM TETRACHLORIDE

B. A. Krentsel*, A. V. Topchiev, and L. G. Sidorova

Several papers have recently appeared concerning a new high polymer, namely isotactic polypropylene prepared by the polymerization of propene in presence of a complex organometallic catalyst $\text{Al}(\text{C}_2\text{H}_5)_3 + \text{TiCl}_4$. TiCl_4 can be successfully replaced by TiCl_3 , which tends to give a polymer of higher crystallinity. On the other hand, the possibility of using trialkylaluminums of higher molecular weight, which are associated with a smaller fire hazard than the highly pyrophoric triethylaluminum, is of considerable interest.

We have therefore studied the possibility of polymerizing propene into polypropylene in presence of $\text{Al}(\text{i-C}_4\text{H}_9)_3 + \text{TiCl}_4$.

EXPERIMENTAL

Triisobutylaluminum was prepared by direct synthesis from isobutene, aluminum, and hydrogen at the Institute of Heteroorganic Compounds (Zakharkin and co-workers). The product used as catalyst component was a colorless mobile liquid of b.p. 55-56° (0.5 mm) and d_4^{20} 0.6; it analyzed as 100% $\text{Al}(\text{i-C}_4\text{H}_9)_3$. The propene was obtained from a pyrolysis plant and analyzed as 88.1% C_3H_6 , 8.2% C_3H_8 , and 3.7% C_2H_4 . The polymerization was carried out in the apparatus that we described previously; it provided for suitable purification of the propene and of the nitrogen used as inert gas. As a medium for the polymerization of propene we used n-pentane.

We give the results of the most characteristic experiments.

Experiment 25 (without pressure). Volume of solvent 300 ml (186 g), concentration of catalyst in solvent 5% (5.68 g of triisobutylaluminum and 3.62 g of titanium tetrachloride), molar ratio $\text{Al}(\text{i-C}_4\text{H}_9)_3 : \text{TiCl}_4 = 1.5 : 1$, temperature of reaction mixture 20°, rate of passage of propene 11 liters/hour, duration of reaction 3 hours. The conversion of propene was 33%. After decomposition of residual catalyst with absolute alcohol, filtration, and washing of the product, we obtained 18 g of solid polymer. The molecular weight of the product, as calculated approximately from the intrinsic viscosity of its solution in decalin at 150°, was 32,800. The melting point of the polypropylene was 154°.

Found %: C 85.71; 85.85; H 14.18; 14.38. Calculated %: C 85.71; H 14.29.

The content of crystalline part in the product was determined by the previously described combined method, which is based on x-ray structure analysis and the determination of infrared absorption spectra.* The content of crystalline region was found to be about 96%.

Experiment 21 (in an autoclave at 6-8 atm). Volume of solvent ("Kalosha" gasoline) 260 ml (186 g), concentration of catalyst in solution 2% (3.72 g), molar ratio $\text{Al}(\text{i-C}_4\text{H}_9)_3 : \text{TiCl}_4 = 1.5 : 1$, temperature of reaction mixture 80°, duration of reaction 1 hour. The solid polypropylene obtained (18.4 g) had molecular weight 26,400 and m.p. 150°.

*The determination was carried out by M. V. Vol'kenshtein's laboratory, and we are greatly indebted to M. V. Vol'kenshtein for this service.

In the experiments at atmospheric pressure on the polymerization of propene it was shown that the yield of solid polymer is greatly dependent on the proportions of catalyst components. As will be seen from Fig. 1, the highest yields are attained at a molar ratio of $\text{Al}(\text{i-C}_4\text{H}_9)_3 : \text{TiCl}_4 = 1.5 : 1$. It should be noted that, as we have stated in an earlier communication, in the preparation of polypropylene in presence of $\text{Al}(\text{C}_2\text{H}_5)_3$ the optimum molar ratio trialkylaluminum : TiCl_4 is considerably higher. It is not yet possible to provide an experimentally based explanation of this fact, but the possibility cannot be excluded that in this case differences in the degrees of dispersity of trialkylaluminums having hydrocarbon groups of different lengths may have a substantial effect.

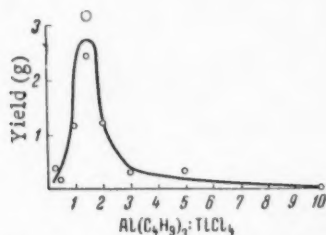


Fig. 1. Effect of the molar ratio $\text{Al}(\text{i-C}_4\text{H}_9)_3 : \text{TiCl}_4$ on the yield of polypropylene; 2% of catalyst (on solvent); solvent n-pentane; 20°; 3 hours.

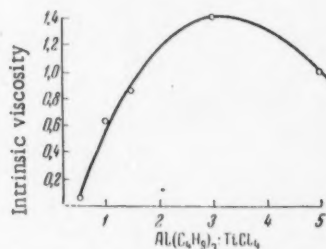


Fig. 2. Relation of the intrinsic viscosity of polypropylene to the molar ratio $\text{Al}(\text{i-C}_4\text{H}_9)_3 : \text{TiCl}_4$.

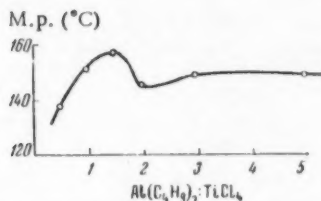


Fig. 3. Relation of the melting point of polypropylene to the molar ratio $\text{Al}(\text{i-C}_4\text{H}_9)_3 : \text{TiCl}_4$.

The proportions of $\text{Al}(\text{i-C}_4\text{H}_9)_3$ and TiCl_4 affect also the molecular weight and melting point of the polymer, as will be seen from the graphs in Figures 2 and 3. Hence, the ratio of catalyst components affects the yield of polymer and can be used as one means of controlling certain properties of solid polypropylene. The high crystallinity of polypropylene prepared from technical propene with the aid of triisobutylaluminum gives us grounds for the view that this catalyst is of great potential importance.

SUMMARY

1. The polymerization of propene into highly crystalline polypropylene was carried out successfully in presence of the complex organometallic catalyst $\text{Al}(\text{i-C}_4\text{H}_9)_3 + \text{TiCl}_4$, which has considerably less fire hazard than $\text{Al}(\text{C}_2\text{H}_5)_3 + \text{TiCl}_4$.

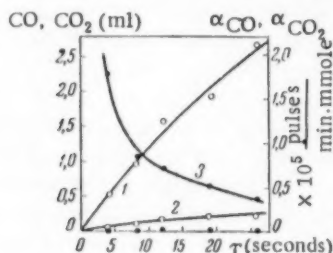
2. The molar ratio of the catalyst components affects the yield and properties of the polypropylene obtained. The optimum molar ratio $\text{Al}(\text{i-C}_4\text{H}_9)_3 : \text{TiCl}_4$ is approximately 1.5 : 1.

MECHANISM OF THE FORMATION OF CARBON DIOXIDE IN THE OXIDATION OF FORMALDEHYDE

A. M. Markevich, R. I. Moshkina, and L. F. Filippova

Nalbandian, Neiman, and co-workers have carried out a series of investigations on the sequence of stages in the oxidation of hydrocarbons, and, in particular, on the ways in which carbon dioxide is formed. In the oxidation of methane [1] and some other hydrocarbons [2] it was shown that CO_2 is formed only partly by the oxidation of

carbon monoxide, most of it being formed in a different way. The CO_2 is probably derived from aldehydes (formaldehyde in the case of methane). Also, it is known that in the oxidation of formaldehyde the main reaction products, water and carbon monoxide, are generally accompanied by CO_2 . It seemed to be desirable to use the method of labeled atoms to obtain direct verification of conclusions, based on work with hydrocarbons, relating to the oxidation of formaldehyde. This was the object of the present work.



Accumulation of CO and CO_2 in the oxidation of formaldehyde.

Original mixture $\text{CH}_2\text{O} : \text{air} =$

$= 1 : 9; 451^\circ; 760 \text{ mm};$

1) accumulation of CO ;

2) accumulation of CO_2 ;

3) specific activity of CO .

The black circles near the axis of abscissae represent specific activity of CO_2 .

analyzed for CO , CO_2 [4], and CH_2O . Carbon oxides were converted into barium carbonate, the activity of which was determined with an end-type counter.

The results of the experiments are represented in the figure, which gives curves for the amounts of CO and CO_2 formed in the reaction and the change in the specific activity α_{CO} with time. It was shown that the specific activity of CO_2 was low; it was not more than 3-5% of that of CO . The results for α_{CO_2} are shown in the figure as black circles near the axis of abscissae. Values of total activity obtained by summation were consistent within 6%.

The results indicate quite clearly that the formation of CO_2 in the oxidation of formaldehyde cannot be associated with the oxidation of CO , because otherwise the points for α_{CO_2} would lie above the curve for α_{CO} [5]. The fact that the specific activity of CO_2 is 3-5% of α_{CO} can be explained either by partial oxidation of CO to CO_2 or, what is more probable, by errors of measurement. The formation of CO_2 is possibly associated with partial heterogeneous oxidation of formaldehyde. Hence, the results of the present work confirm the correctness of conclusions concerning the formation of carbon dioxide reached in the investigation of the oxidation of methane.

SUMMARY

The ways in which carbon dioxide is formed in the oxidation of formaldehyde at 451° were investigated. It was shown that not more than 3-5% of the CO₂ formed can arise by the oxidation of CO. The bulk (95-97%) of the CO₂ is formed directly from formaldehyde.

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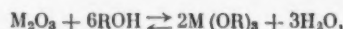
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SYNTHESIS OF TRIALKYL VANADATES AND TRIALKYL ANTIMONITES

M. G. Voronkov and Iu. I. Skorik

There are indications in the literature that trialkyl vanadates $OV(OR)_3$ [1, 2] and trialkyl antimonites $Sb(OR)_3$ [3] can be prepared by the reaction of V_2O_5 and Sb_2O_3 , respectively, with alcohols:



in which $M = Sb$ or OV . Our attempts to reproduce these results were not very successful. When V_2O_5 or Sb_2O_3 was boiled with ethyl or butyl alcohol under various conditions designed to remove water formed in the reaction (water trap, anhydrous $CuSO_4$ cartridge, ethyl silicate, etc.), the formation of trialkyl antimonites did not occur at all, and the yields of trialkyl vanadates were very low.

We later prepared trialkyl vanadates and trialkyl antimonites very readily and simply by the reaction of $VOCl_3$ and $SbCl_3$, respectively, with alcohols in presence of ammonia:



In this way we synthesized ethyl and butyl esters of vanadic, antimonous, and also phosphorous acids in yields of up to 80%.

It must be pointed out that in the reaction of $VOCl_3$ with sodium ethoxide no triethyl vanadate is formed [1]. Also, in the case of the synthesis of ortho-esters of acids of other elements of Group V, the proposed method of synthesis from acid chlorides and alcohols is more convenient than that in which sodium alkoxides are used for the binding of HCl [1, 4-6].

EXPERIMENTAL

Starting Materials. Vanadyl chloride was prepared in 74% yield by boiling anhydrous V_2O_5 with excess of thionyl chloride until SO_2 ceased to be evolved [7] and was purified by distillation; b.p. 126° (758 mm). Commercial antimony trichloride was purified by vacuum distillation; b.p. 111° (20 mm); m.p. 73° . Ethyl alcohol was made absolute by boiling it with ethyl silicate in presence of sodium ethoxide; it was then distilled through a column. Butyl alcohol was distilled through a column over potassium. The physical constants of these substances were in accord with the literature [8].

Triethyl Vanadate. Absolute ethyl alcohol (350 ml) was introduced into a three-necked flask fitted with mercury-sealed mechanical stirrer, dropping funnel, and tubes for the entry and exit of gases. The alcohol was stirred and cooled with snow while 86.7 g (0.5 mole) of $VOCl_3$ was dropped in. The solution was stirred and cooled while dry (dried with solid KOH) ammonia was passed in from a cylinder until evolution of heat in the reaction mixture ceased. Cooling was then stopped, and the passage of ammonia was continued for a further 50 minutes. The precipitate of ammonium chloride was filtered off in an atmosphere of dry ammonia and was washed with absolute alcohol. Alcohol was distilled from the filtrate, and the residue was vacuum-distilled. The yield of triethyl vanadate, b.p. $98-101^\circ$ (16 mm), was 55.6 g (55%). After redistillation it had b.p. 82.5° (5 mm) and 91° (11 mm); d_{20}^{20} 1.167, n_D^{20} 1.5103. Triethyl vanadate is a yellowish-orange liquid, extremely readily hydrolyzed by atmospheric moisture and decomposed by irradiation or when distilled at a residual pressure of more than 20 mm.

Found %: V 25.15; 24.68. $C_6H_{15}O_4V$. Calculated %: V 25.21.

The literature [1] gives b.p. 98.5° (16 mm) and d_4^{15} 1.167. In a similar way we prepared also tributyl vanadate; b.p. 121° (1 mm), 131° (3.5 mm), and 153° (7 mm); d_4^{20} 1.031; n_D^{20} 1.4898. The literature [1] gives b.p. 175° (22 mm). Tributyl vanadate is a yellow very readily hydrolyzable liquid which decomposes when distilled.

Found %: V 17.41; 17.38. $C_{12}H_{27}O_4V$. Calculated %: V 17.80.

Triethyl Antimonite. The synthesis was carried out in the apparatus described. Dry ammonia was passed through a cooled, stirred solution of 342.2 g (1.5 moles) of antimony trichloride and 550 ml of absolute ethyl alcohol. When the evolution of heat stopped, cooling was discontinued and ammonia was passed further for 30 minutes. The precipitate of ammonium chloride was filtered off in a stream of dry ammonia and was washed with absolute alcohol. Alcohol was distilled from the filtrate, and the residue was vacuum-distilled. The yield of triethyl antimonite, b.p. 93° (10 mm), d_4^{20} 1.526; n_D^{20} 1.4983-231.2 g (60%); it is a colorless extremely readily hydrolyzable liquid.

Found %: Sb 47.47; 47.55. $C_6H_{15}O_3Sb$. Calculated %: Sb 47.39.

The literature [6] gives b.p. 94-95° (10 mm) and n_D^{20} 1.4946. In exactly the same way we prepared tributyl antimonite in 80% yield. It had b.p. 144° (10 mm), d_4^{20} 1.280; n_D^{20} 1.4799, (the literature [5] gives b.p. 138.5-139.5° (6 mm) and d_4^{20} 1.2804).

Found %: Sb 35.51; 35.59. $C_{12}H_{27}O_3Sb$. Calculated %: Sb 35.70.

SUMMARY

A method is proposed for the synthesis of trialkyl vanadates and trialkyl antimonites by reaction of $VOCl_3$ and $SbCl_3$, respectively, with alcohols in presence of ammonia.

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COMPOSITION OF THE PRODUCTS IN THE SYNTHESIS OF AMINES FROM CARBON MONOXIDE, HYDROGEN, AND AMMONIA

A. N. Bashkirov, Iu. B. Kagan, and G. A. Kliger

We have previously [1] carried out the direct synthesis of alkylamines from carbon monoxide, hydrogen, and ammonia in presence of fused iron catalysts. The products of the synthesis contained up to 25% of aliphatic amines. We carried out further investigations with the object of improving the catalysts. As a result we found an active, stable, and relatively selective iron catalyst promoted by amphoteric and basic oxides introduced simultaneously in equimolecular amounts. In presence of this catalyst under optimum conditions, 1 cu.m of treated gas gave 120.0 g of synthesis products (apart from water), of which 54.0% consisted of alkylamines (made up of 33.0% of liquid amines and 21.0% of gaseous amines). In the present paper we give the results of the analysis of the liquid alkylamines.

EXPERIMENTAL

The product studied was obtained in the course of a 500-hour run over the catalyst. The liquid amines isolated from this product contained 88.5% of primary, 8.45% of secondary, and 3.05% of tertiary amines; the relative amounts of these were determined by potentiometric titration [1]. The results of the fractionation of these amines through an efficient column having a glass filling are given in Table 1.

TABLE 1

Results of Fractionation through a Column for Liquid Amines Obtained in the Synthesis From CO, H₂, and NH₃

Boiling range of fraction (°C)	Content of fraction (%)	Boiling range of fraction in °C (p in mm)	Content of fraction (%)	Boiling range of fraction in °C (p in mm)	Content of fraction (%)
Up to 77.5	2,99	104,1—130,5	8,21	86,2—87,6 (32)	2,69
77,5—77,6	4,56	130,5—130,7	4,17	87,0—103,8 (32)	4,08
77,6—104,0	6,25	130,7—154,7	11,50	103,8—105,0 (32)	1,38
104,0—104,1	6,13	154,7—155,0	6,10	105,0—119,0 (32)	2,83
		69,0—86,2 (32)	2,04	119,0—121,5 (32)	1,08

Fractions corresponding in boiling point to primary aliphatic amines were characterized by their physical constants, in some cases by the melting points of their picrates, and by elementary analysis. The values so found, which agreed with those in the literature, are given in Tables 2 and 3.

Comparison of the data given in Tables 2 and 3 shows that the fraction of b.p. 77.5–77.6° was butylamine, that of 104.0–104.1° was pentylamine, that of b.p. 130.4–130.6° was hexylamine, that of b.p. 154.7–155° was heptylamine, and that of b.p. 86.2–87.0° (32 mm) was octylamine.

The residue after the fractionation through a column was vacuum-fractionated into narrow fractions from a Claisen flask. The results of the fractionation and the analysis of the fractions are given in Table 4.

TABLE 2

Results of the Elementary Analysis of Certain Fractions

Boiling range of fraction in °C (p in mm)	Expected amine	Found (%)			Calculated (%)		
		C	H	N	C	H	N
77,5—77,6	<i>n</i> -C ₄ H ₉ NH ₂	65,30	15,00	19,31	65,74	15,05	19,21
104,0—104,1	<i>n</i> -C ₅ H ₁₁ NH ₂	68,96	15,04	16,08	68,96	14,94	16,10
130,5—130,7	<i>n</i> -C ₆ H ₁₃ NH ₂	71,19	14,80	13,89	71,28	14,85	13,87
154,7—155,0	<i>n</i> -C ₇ H ₁₅ NH ₂	73,00	14,68	12,61	73,04	14,80	12,16
86,2—87,0/32	<i>n</i> -C ₈ H ₁₇ NH ₂	74,49	14,79	10,59	74,42	14,73	10,85
103,8—105,0/32	<i>n</i> -C ₉ H ₁₉ NH ₂	76,54	14,67	8,71	75,52	14,69	9,79
119,0—121,5/32	<i>n</i> -C ₁₀ H ₂₁ NH ₂	77,05	14,64	7,96	76,43	14,65	8,92

TABLE 3

Physical Constants of Certain Fractions

Expected amine	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	M. p. of picrate (°C)	Literature reference
Butylamine	77,5—77,6	0,7409	1,4018	148,5—149,0*	[2—5]
Pentylamine	104,0—104,1	0,7623	1,4104	139,5—140,0	[4, 6, 7]
Hexylamine	130,4—130,6	0,7629 ²⁵	1,4182	—	[8]
Heptylamine	154,7—155,0	0,7780	1,4238	123,5**	[6, 9—11]
Octylamine	86,2—87,0/32	0,7759 ²⁷	1,4292	—	[4, 12]

* In admixture with butylamine picrate there was no depression of melting point.

** In admixture with picric acid there was a depression of melting point.

TABLE 4

Results of the Fractionation of the Residue and Analysis of the Fractions so Obtained

Boiling range of fraction (°C at 2 mm)	Content of fraction (%)	d_4^{20}	n_D^{20}	Found (%)			
				C	H	N	C+H+N
90—110	6,10	0,8480	1,4493	76,89	13,81	8,99	99,59
110—130	4,38	0,8502	1,4521	76,22	14,22	8,67	99,11
130—150	4,10	0,8530	1,4549	77,21	14,01	8,29	99,52
150—170	3,72	0,8540	1,4584	77,95	14,13	7,63	99,71
160—190	3,86	0,8548	1,4622	78,70	14,17	7,05	99,92
Residue + losses	13,88	—	—	—	—	—	—

It follows from Table 4 that fractions boiling above 90° (2 mm) are aliphatic amines having 11–20 and more carbon atoms in their molecules. The product remaining after the separation of aliphatic amines contained hydrocarbons and about 15% of oxygen compounds (alcohols and compounds containing the carbonyl group).

SUMMARY

1. In reaction between CO, H₂, and NH₃ in presence of a fused iron catalyst, aliphatic amines (mainly primary) having carbon chains of 1–20 atoms and more are formed.

2. Among the liquid products of the synthesis, butylamine, pentylamine, hexylamine, heptylamine, and octylamine were identified.

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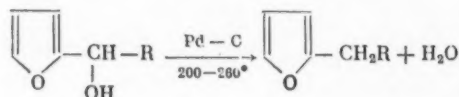
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HYDROGENATION OF α -ALKYLFURFURYL ALCOHOLS OVER AN Ni - ZnO CATALYST

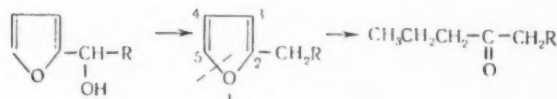
N. I. Shuikin and I. F. Bel'skii

The hydrogenation of α -alkylfurfuryl alcohols may proceed differently according to the nature of the catalyst and the reaction conditions (liquid or vapor phase). In the liquid phase over Raney nickel [1] and platinum promoted with iron salts [2] α -alkylfurfuryl alcohols are converted in high yield into the corresponding alcohols of the tetrahydrofuran series. We showed recently [3] that the primary reaction in the vapor-phase hydrogenation of α -alkylfurfuryl alcohols over palladized charcoal at 200-260° is not the hydrogenation of double bonds in the ring, but reduction of the hydroxy group with formation of 2-alkylfurans:



However, in compounds of the type $\text{R}-\underset{\text{OH}}{\text{CH}}-\text{Alk}$, in which R is tetrahydrofuryl or alkyl, the link between the carbon atom and the hydroxy group is quite stable and is not broken under the action of hydrogen over a palladium catalyst in the temperature range indicated.

We have now investigated the vapor-phase hydrogenation of α -alkylfurfuryl alcohols over an Ni-ZnO catalyst and have found that, like palladized charcoal, this catalyst selectively promotes, as primary reaction, the reduction of the hydroxy group in α -alkylfurfuryl alcohols and leaves the double bonds of the furan ring untouched. However, unlike palladium, which is of low activity with respect to the hydrogenolysis of the furan ring, Ni-ZnO is very efficient in promoting this reaction, which proceeds with exclusive rupture of the C-O bond that is not adjacent to the alkyl group. As a result, the alkylfurans formed by the reduction of α -alkylfurfuryl alcohols are hydrogenolyzed at the C-O bond in the 1,5-position with formation of aliphatic ketones:



The relative contents of ketones and alkylfurans in the reaction products depend on the temperature and the rate of passage of the substance over the catalyst. At a constant space velocity of 0.1 hour⁻¹ the catalyzates from α -methyl- and α -ethyl-furfuryl alcohols obtained by hydrogenation at 200° contained approximately equal amounts of the corresponding alkylfurans and ketones, whereas the catalyzate from α -isopropylfurfuryl alcohol, obtained at 250°, contained only 2-methyl-4-heptanone.

Like palladized charcoal, Ni-ZnO is quite unable to bring about the reduction of the hydroxy group of secondary alcohols. Thus, 2-pentanol, passed over Ni-ZnO in hydrogen at 250°, is only dehydrogenated with formation of 2-pentanone in 65% yield. Hence, the tendency for the hydroxy group of α -alkylfurfuryl alcohols to undergo catalytic reduction is determined by the effect of the aromatic system of the furan ring, which is conjugated with the C-O bond.

EXPERIMENTAL

Ni-ZnO containing 30% of nickel was prepared by coprecipitation of nickel and zinc hydroxides from a solution of the nitrates with ammonia, and reduction with hydrogen at 200-320°. α -Methyl-, α -ethyl-, and α -isopropyl-furfuryl alcohols were synthesized from 2-furaldehyde and alkyl halides by the Grignard reaction [3]. The reaction products were dried with calcium chloride and fractionated through an efficient column. The catalyzates obtained by a single passage of the α -alkylfurfuryl alcohols over the catalyst at a space velocity of 0.1 hour⁻¹ contained not only the main reaction products, the corresponding alkylfurans and aliphatic ketones, but also 10-15% of unchanged alcohol and about 10% of high-boiling products. The conditions and results of the experiments are shown in the table.

TABLE

Products of the Hydrogenation of α -Alkylfurfuryl Alcohols Over Ni-ZnO

α -Alkylfurfuryl Alcohol	Temperature (°C)	Reaction products (% on alcohol that reacted)
α -Methylfurfuryl alcohol	200	2-Ethylfuran (47)
		3-Heptanone (45)
α -Ethylfurfuryl alcohol	200	2-Propylfuran (52)
		4-Heptanone (40)
α -Isopropylfurfuryl alcohol	250	2-Methyl-4-heptanone (88)

SUMMARY

In the hydrogenation of α -alkylfurfuryl alcohols in the vapor phase over an Ni-ZnO catalyst at 200-250°, reduction of the hydroxy group occurs with formation of 2-alkylfurans; these compounds are converted, partially or completely according to the temperature, into the corresponding aliphatic ketones as a result of the hydrogenolysis of the ring at the C-O bond.

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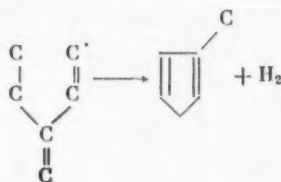
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CATALYTIC DEHYDROCYCLIZATION OF 2-ETHYL-1,3-BUTADIENE

N. I. Shuikin and T. I. Naryshkina

As is well known, a fairly detailed study has now been made of the catalytic dehydrocyclization of alkanes having chains of six or more carbon atoms, which results in the formation of aromatic hydrocarbons. The authors and others [1, 2] showed recently that an analogous reaction may occur with formation of cyclopentanes. Also, Kennedy and Hetzel [3] and Shuikin and co-workers [4-6] showed that piperylene can undergo ring-closure into cyclopentadiene at about 600° in presence of various catalysts. The maximum yield of cyclopentadiene in this reaction attains 20% on the amount of piperylene taken. We further showed [7] that a close homolog of piperylene, 3-methyl-1,3-pentadiene, has a high tendency to undergo dehydrocyclization and can undergo ring-closure with formation of methylcyclopentadiene in 47.5% yield on the amount of diene taken. This reaction is favored by reduction of pressure to 20 mm, which results in considerable suppression of side reactions, including the polymerization of the original and final dienes. The most effective catalysts were alumina-chromia-potassia and 5% platinized charcoal.

In the present work we have shown that 2-ethyl-1,3-butadiene is also able to undergo cyclization with formation of methylcyclopentadiene in yields of up to 38%:



EXPERIMENTAL

2-Ethyl-1,3-butadiene was obtained together with 3-methyl-1,3-pentadiene by the dehydration of 2-ethyl-3-buten-2-ol [8] over magnesium sulfate. 2-Ethyl-1,3-butadiene was isolated by precision fractionation; it had b.p. 65-66° (756 mm), n_D^{20} 1.4250 and d_4^{20} 0.7154. The Raman spectrum of 2-ethyl-1,3-butadiene contained the following frequencies.*

$\Delta\nu$ (cm⁻¹): 233 (2 b), 290 (0), 342 (0), 400 (1), 424 (1), 472 (1 b), 534 (6 b), 556 (1), 680 (2 b), 702 (1), 739 (2), 764 (6 b), 799 (1), 900 (7 b), 951 (1), 993 (1), 1001 (1), 1030 (1), 1067 (2), 1088 (8 b), 1239 (5), 1258 (5), 1294 (10), 1328 (2 b), 1360 (1 b), 1422 (10 b), 1452 (3 b), 1609 (1), 1634 (10 b), 1673 (5), 2857 (1), 2879 (8), 2909 (8), 2939 (8), 2965 (8), 3007 (10), 3084 (7 b).

The dehydrocyclization of 2-ethyl-1,3-butadiene was carried out at 550-600° at reduced pressure (20 mm) in presence of an alumina-chromia-potassia catalyst [6] and also of 5% Pt-charcoal. In each experiment we took 25 ml (17.9 g) of the hydrocarbon, which was passed into the reaction zone at a rate of 1.0 hour⁻¹. The catalyzates were analyzed for methylcyclopentadiene by the colorimetric method proposed by Afanas'ev [9] for the determination

*The Raman spectrum of 2-ethyl-1,3-butadiene was determined by Iu. P. Egorov and is published for the first time; the same worker in collaboration with G. K. Gaivoronskaia carried out the Raman analysis of the fractions, and we are greatly indebted to them.

of cyclopentadiene and used by us for the determination of methylcyclopentadiene [7]. The catalyzates were then fractionated through a highly efficient column into fractions, which were subjected to spectrum analysis. The gaseous products were analyzed in an Orsat-Lunge apparatus and, in greater detail, by the chromatographic method [10]. The results of experiments on the dehydrocyclization of 2-ethyl-1,3-butadiene are given in Table 1.

TABLE 1

Dehydrocyclization of 2-Ethyl-1,4-butadiene

Catalyst	Temperature of experiment	Yield of catalyzate (%)	n_D^{20} of catalyzate	Content of methylcyclopentadiene		Coke formation (%)
				(% on catalyzate)	(% on original ethylbutadiene)	
$Al_2O_3 + Cr_2O_3 + K_2O$	550	82.7	1.4520	38	32	11
$Al_2O_3 + Cr_2O_3 + K_2O$	600	76.8	1.4530	50	38	13
5% Pt-charcoal	550	88.9	1.4515	29	26	—
5% Pt-charcoal	600	81.0	1.4525	34	28	—

As shown in Table 1, the yield of methylcyclopentadiene in presence of an alumina-chromia-potassia catalyst at 600° was 38%, calculated on the original hydrocarbon.

In order to determine the composition of the reaction products, 50 g of the combined catalyzate was fractionated through a column. The fractionation results are given in Table 2.

TABLE 2

Results of the Fractionation of the 2-Ethyl-1,3-butadiene Catalyzate

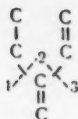
Fraction	Boiling range (°C at 750 mm)	Amount of fraction (%)	Properties of fraction	
			n_D^{20}	d_4^{20}
I	34-67	14.8	1.4270	0.7282
II	67-72	34.4	1.4360	0.7459
III	72-78	34.0	1.4570	0.8195
	Residue	15.2	—	—
	Losses	1.6	—	—

According to Ramanspectrum analysis, Fraction I consisted mainly of cyclopentadiene (about 70%), isoprene, 2-ethyl-1,3-butadiene, and 3-methyl-1-pentene. Fraction II contained equal amounts of methylcyclopentadiene and the original 2-ethyl-1,3-butadiene, and also a very small amount of a C_6 alkene. Fraction III contained mainly methylcyclopentadiene with some benzene (about 10%) and, apparently, 3-methyl-1,3-pentadiene. The residue from the fractionation was a hard glassy mass, close in composition to the polymer of methylcyclopentadiene.

Found %: C 88.1; H 9.4. $(C_6H_8)_x$. Calculated %: C 89.9; H 10.1.

Analysis of the group composition of the gaseous products in an Orsat-Lunge apparatus showed that they consisted of hydrogen (25%), unsaturated hydrocarbons (30%), and paraffins (45%). By more detailed chromatographic analysis of the gaseous products we found methane (3%), ethane (32%), ethylene (19%), propane (9%), propene (10%), and butadiene (2.0%). From the results of the analysis of the reaction products it is clear that under the given conditions not only the dehydrocyclization of 2-ethyl-1,3-butadiene occurs, but also demethylation (of the original hydrocarbon and also of the methylcyclopentadiene formed), partial hydrogenation, isomerization, and hydrocracking.

The presence of a large amount of C_2 hydrocarbons in the gaseous products leads us to suppose that the breakdown of 2-ethyl-1,3-butadiene proceeds preferentially at the 1,2- and 2,3-linkages:



SUMMARY

1. The dehydrocyclization of 2-ethyl-1,3-butadiene was investigated. It was shown that it can undergo ring-closure with formation of methylcyclopentadiene in 38% yield, calculated on the original hydrocarbon.
2. Comparison of the results of the present investigation with the results that we obtained previously on the dehydrocyclization of alkadienes shows that C_6 hydrocarbons having a branched carbon-chain have an enhanced tendency to undergo dehydrocyclization, as compared with linear piperylene.

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TRANS CONFIGURATION OF 1,2-DISILYLETHYLENES

Iu. P. Egorov, L. A. Leites, and V. F. Mironov

In previous papers [1-3] we described for the first time the syntheses of 1,2-bis(trichlorosilyl)ethylene [1,1,1,4,4,4-hexachloro-1,4-disilabut-2-ene] and 1,2-bis(trimethylsilyl)ethylene (2,2,5,5-tetramethyl-2,5-disilahept-3-ene) and the Raman spectrum of the second of these compounds. We suggested tentatively [3] that the broadening of the double bond frequency observed in this spectrum by 20 cm^{-1} may be explained by cis-trans isomerism. However, already at that time we had doubts about the correctness of this supposition because of the steric difficulties found when we attempted to make a space model of the cis form of this molecule.

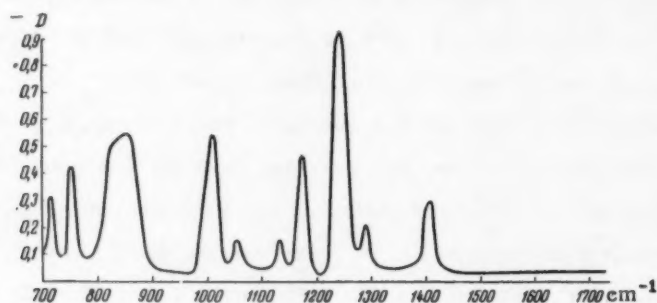


Fig. 1.

Batuev and others [4] described the Raman spectrum of 1,2-bis(trichlorosilyl)ethylene, and on the basis of the presence in this spectrum of two widely spaced lines of equal intensity in the double bond region (1559 and 1602 cm^{-1}) and also of closely spaced or double lines (1282 and 1297 cm^{-1} , 2975 cm^{-1} (db), and others) they concluded

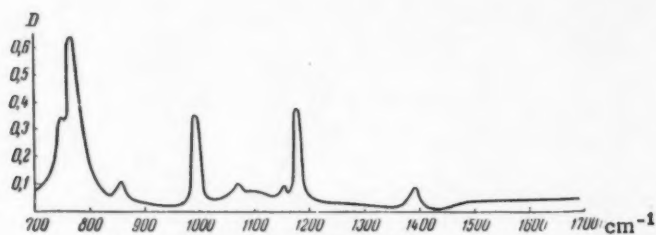
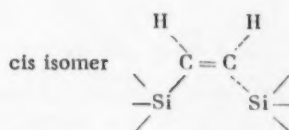


Fig. 2.

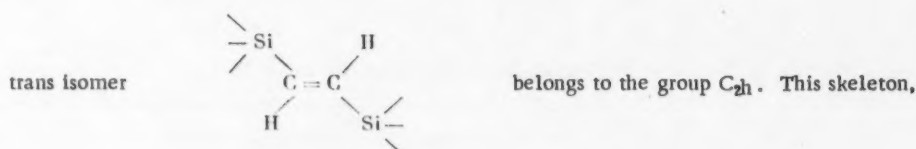
that "these phenomena very definitely indicate that the substance under investigation is a mixture of cis and trans isomers in approximately equal amounts." This assertion compelled us to return to this question and examine it more carefully. We studied the infrared spectra of these two compounds and compared them with the Raman spectra, determined previously [3, 4]. The infrared spectra were determined on a Soviet IKS-11 spectrograph. The determinations were made on the pure substances and on their solutions in carbon disulfide and tetrachloroethylene.

The absorption curves for $(\text{CH}_3)_3\text{SiCH}=\text{CHSi}(\text{CH}_3)_3$ and $\text{Cl}_3\text{SiCH}=\text{CHSiCl}_3$ are given in Figures 1 and 2 respectively.

The flat skeleton of each molecule $\text{—SiHC}=\text{CHSi—}$ is analogous to dichloroethylene, and the



belongs to the point symmetry group C_{2v} , whereas the



like that of dichloroethylene, should have 12 natural vibrations, and in the centrosymmetrical trans configuration, which is subject to alternative prohibition, 6 vibration frequencies (5 of type A_g and 1 of type B_g) should be active only in the Raman spectrum, and the other 6 (2 of type A_i and 4 of type B_i) only in the infrared spectrum [5]. For the cis configuration with C_{2v} symmetry, alternative prohibition is absent and various frequencies (e.g., the $\text{C}=\text{C}$ valence vibration) should appear in both spectra.

TABLE 1

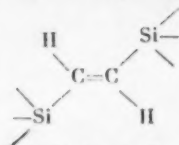
Vibration Frequencies of $\text{Cl}_3\text{SiCH}=\text{CHSiCl}_3$

Infrared spectrum	Raman spectrum	Assignment of frequencies
748 (w)	743 (1)	Completely sym. $\nu_{\text{Si}-\text{C}}$
769 (s)	757 (0)	Antisym. $\nu_{\text{Si}-\text{C}}$
	774 (0)	$\rho_{\text{HC}=\text{C}}$
853 (w)	—	
995 (m)	—	
1067 (w)	—	
1153 (w)	—	$2\nu_{\text{Si}-\text{Cl}}$ (antisym.)
1181 (m)	—	Antisym. $\delta_{\text{HC}=\text{C}}$
—	1282 (6)	Completely sym. $\delta_{\text{HC}=\text{C}}$
—	1297 (6)	
1395 (m)	—	
	1559 (5)	$\nu_{\text{C}=\text{C}}$
	1602 (5)	

In Tables 1 and 2 we compare the infrared and Raman spectra of 1,2-bistrichlorosilyl- and 1,2-bis(trimethylsilyl)-ethylenes and give the most probable assignment of the frequencies. It will be seen from an examination of Tables 1 and 2 that not one of the natural frequencies in the infrared spectrum belonging to the vibrations of the flat skeleton is observed in the Raman spectrum. Exceptions are the frequencies 840, 1250, and 1413 cm^{-1} , which appear in both the infrared and Raman spectra of 1,2-bis(trimethylsilyl)ethylene and arise from the vibrations of the group $(\text{CH}_3)_3\text{Si}$ [6], which has its own symmetry C_{3v} , to which alternative prohibition does not apply. It is particularly notable that the infrared spectra of the two molecules do not contain absorption bands in the region $1650\text{--}1550\text{ cm}^{-1}$, corresponding to the $\text{C}=\text{C}$ valence vibration. All this forms a reliable proof of the centrosymmetric trans configuration of the molecules of these compounds.

We made Stuart models of these molecules and again showed, in this case extremely clearly, that the existence

of the *cis* form, particularly of 1,2-bistrichlorosilylethylene, is impossible because of steric hindrance. In view of this it is very probable that the splitting of frequencies noted, by Batuev and others, in the Raman spectrum of 1,2-bistrichlorosilylethylene can be explained by rotational isomerism (differing dispositions of the chlorine atoms



with respect to the plane $\left(\begin{array}{c} \text{H} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{H} \end{array} \right)$ on analogy with the splitting of frequencies in compounds of the type $\text{CH}_2=\text{CH}-\text{O}-\text{R}$ [7]. Broadening of the double bond frequencies in the Raman spectrum of 1,2-bis(trimethylsilyl)ethylene can also be explained by rotational isomerism of the methyl groups, but as the broadening and splitting of other lines in the spectrum of this molecule are not observed it is also possible that the phenomenon is due to Fermi resonance.

TABLE 2

Vibration Frequencies of $(\text{CH}_3)_3\text{SiCH}=\text{CHSi}(\text{CH}_3)_3$

Infrared spectrum	Raman spectrum	Assignment of frequencies
717 (m)	—	Antisym. $\nu_{\text{Si}-\text{C}}$
756 (s)	—	
824—862 (s)	789 (5)	Antisym. δ_{CH} in Si-attached CH_3
	842 (10)	
	882 (2)	
1012 (s)	—	$\rho_{\text{C}=\text{CH}}$
1057 (w)	—	Antisym. $\delta_{\text{CH}=\text{C}}$
1135 (w)	—	
1175 (vs)	—	Completely sym. and doubly degenerated δ_{CH} in Si-attached CH_3
1250 (vs)	1248 (15) } 1258 (15) }	
1293 (w)	1295 (40 sh)	Completely sym. $\delta_{\text{CH}=\text{C}}$
	1367 (2)	
1413 (m)	1412 (20 b)	Antisym. δ_{CH} in Si-attached CH_3
1512 (w)	—	
—	1551—1571 (20 v.b)	$\nu_{\text{C}=\text{C}}$

SUMMARY

1. The infrared spectra of 1,2-bistrichlorosilyl- and 1,2-bis(trimethylsilyl)-ethylenes were determined in the region $700\text{--}1700\text{ cm}^{-1}$.
2. It was shown that these molecules have the centrosymmetrical *trans* configuration.

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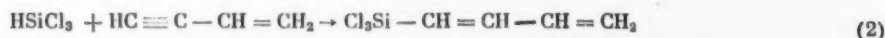
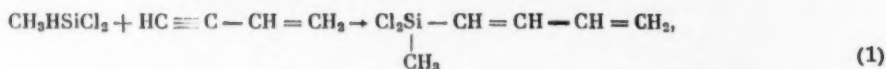
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ADDITION OF 1-BUTEN-3-YNE TO SILANES CONTAINING SILICON-ATTACHED HYDROGEN

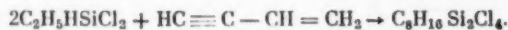
A. D. Petrov and S. I. Sadykh-Zade

Shostakovskii and Kochkin [1] recently studied the addition of acetylene at 170-180° to methyl- and ethyl-silanes containing silicon-attached hydrogen. In presence of platinized charcoal the yields of alkyldichlorovinylsilanes did not exceed 3.2-3.6%; in presence of palladized alumina they were raised to 23-30%. In 1954 we investigated the addition of 1-buten-3-yne to silanes containing silicon-attached hydrogen at 150-160° both over platinized charcoal and over palladized calcium carbonate. In both cases the reaction went, but under these conditions the resulting 1,3-butadienylsilanes polymerized with formation of viscous liquid polymers. As we did not then succeed in isolating individual compounds, we did not publish these observations. An attempt to carry out the desired reaction at low temperatures with these catalysts was also unsuccessful.

In the present investigation we have succeeded in finding a catalyst capable of bringing about the addition at room temperature, of 1-buten-3-yne to silanes containing silicon-attached hydrogen, and the 1,3-butadienylsilanes obtained in this way polymerized only to a slight extent. The catalyst found was a homogeneous platinum preparation, namely a 0.1 N solution of H_2PtCl_6 in isopropyl alcohol. With this catalyst we carried out the reactions:



The yields were 50% and 40% respectively on the amount of the silane that reacted. It is interesting that in the case of $C_2H_5HSiCl_2$ there was again reaction predominantly in one direction with a yield of product (bis(dichloroethylsilyl)butene) of about 50%, but the course of the reaction was different:



We established that the direction of addition of dichloromethylsilane was as indicated above by determination of the spectrum of methylated 1,3-butadienyldichloromethylsilane and comparison with the spectrum of the 1,3-butadienyltrimethylsilane that we prepared previously [2] by another reaction.

EXPERIMENTAL

1,3-Butadienyldichloromethylsilane. A 500-ml rotating autoclave was charged with a mixture of 115.5 g dichloromethylsilane, 56 g of 1-buten-3-yne, and 1.5 ml of the above-described platinum catalyst. The autoclave was rotated at room temperature for 18 hours. The weight of reaction mixture unloaded was 160 g. Unchanged dichloromethylsilane and 1-buten-3-yne were distilled off, and the reaction product (60 g) was fractionated at a residual pressure of 30 mm. The fractions collected were Fraction I, b.p. 34-60°, 3 g; Fraction II, b.p. 60-60.5°, 30 g; Fraction III, b.p. 60.5-140°, 7 g. The residue (20 g) was a polymer that could not be distilled without decomposition. Fraction II had n_D^{20} 1.4820; d_4^{20} 1.0730; found MR 44.37; calculated MR 42.49; yield 50% (on the dichloromethylsilane that reacted).

Found %: C 36.52; 36.57; H 4.97; 5.06; Si 16.79; 17.18. $C_5H_8SiCl_2$. Calculated %: C 35.94; H 4.79; Si 16.74.

The methylation product had the following properties: b.p. 113.5-114° (750 mm); n_D^{20} 1.4478; d_4^{20} 0.7540. Its adduct with maleic anhydride had m.p. 124°. Its Raman spectrum was identical with that of 1,3-butadienyltrimethylsilane obtained previously by another method [2]. Raman spectrum: 149 (2), 169 (0), 202 (6), 221 (5), 262 (1 b), 358 (4), 464 (4), 579 (0), 598 (1), 620 (10), 688 (114), 725 (4), 772 (1), 840 (4 b), 907 (4), 933 (4), 968 (1), 1130 (8 b), 1189 (1 b), 1233 (7), 1250 (2), 1285 (9), 1302 (6), 1410 (6), 1628 (10), 2898 (8), 2960 (8), 3003 (4), 3087 (3).

1,3-Butadienyltrichlorosilane. After reaction between 97.5 g of HSiCl_3 and 46.6 g of 1-buten-3-yne under similar conditions, and removal of unchanged reactants by distillation, we obtained 10 g of reaction products. Vacuum fractionation (30 mm) gave Fraction I, b.p. 45-53°, 1.5 g; Fraction II, b.p. 53-54°, 4 g (40% on the amount of trichlorosilane that reacted). Fraction II had n_D^{20} 1.4740; d_4^{20} 1.1657.

Bis(dichloroethylsilyl)butene. After reaction between 129 g of $\text{C}_2\text{H}_5\text{HSiCl}_2$, 56 g of 1-buten-3-yne in presence of 1.5 ml of the platinum catalyst under similar conditions, and removal of unchanged reactants by distillation, we obtained 65 g of reaction products. Vacuum fractionation (1 mm) gave Fraction I, b.p. 45-92°, 1.5 g; Fraction II, b.p. 92-93°, 30 g; Fraction III, b.p. 93-160°, 10 g. The residue was a polymer. Fraction II had n_D^{20} 1.4890; d_4^{20} 1.1819; found MR 75.75; calculated MR 75.0.

Found %: C 31.83; H 5.41; Si 18.43. $\text{C}_8\text{H}_{16}\text{Si}_2\text{Cl}_4$. Calculated %: C 30.98; H 5.16; Si 18.07.

Its ethylation product had the following properties: b.p. 103-104° (1 mm); n_D^{20} 1.4780; d_4^{20} 0.8674.

The exact structure of the bis(dichloroethylsilyl)butene is under investigation.

We thank Iu. A. Egorov for the spectrum determinations.

SUMMARY

1,3-Butadienylchlorosilanes were synthesized for the first time by reaction at room temperature between 1-buten-3-yne and silanes containing silicon-attached hydrogen in presence of a homogeneous platinum catalyst.

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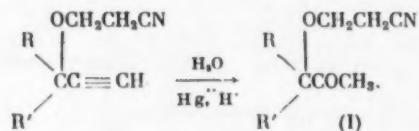
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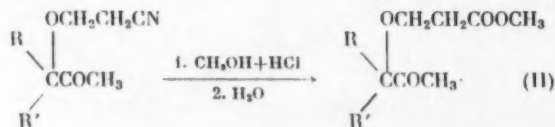
HYDRATION OF 2-CYANOETHYL ETHERS OF ACETYLENIC ALCOHOLS. ALCOHOLYSIS OF THE HYDRATION PRODUCTS

I. N. Nazarov and G. A. Shvekhgeimer

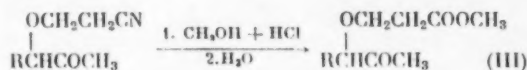
We have previously described the hydration of the 2-cyanoethyl ether of 2-methyl-3-butyne-2-ol in presence of mercuric sulfate and sulfuric acid [1]. In the present investigation we carried out the hydration of various 2-cyanoethyl ethers of secondary and tertiary acetylenic alcohols:



The resulting 2-cyanoethyl ethers [1], and also the 2-cyanoethyl ether of 3-hydroxy-3-methyl-2-butanone synthesized previously [1], were subjected to alcoholysis with methanolic hydrogen chloride at room temperature [2]. The 2-cyanoethyl ethers of hydroxy ketones (I), obtained by the hydration of 2-cyanoethyl ethers of tertiary acetylenic alcohols, were converted under the conditions of alcoholysis into the corresponding 2-(methoxycarbonyl)-ethyl ethers (II) in yields of 60-90%:



In contrast, the alcoholysis of 2-cyanoethyl esters of hydroxy ketones prepared from 2-cyanoethyl esters of secondary acetylenic alcohols was accompanied by side reactions even under very mild conditions, and the expected 2-(methoxycarbonyl)ethyl ethers (III) were formed in very low yields (about 20%):



EXPERIMENTAL

Hydration of 2-Cyanoethyl Ethers of Acetylenic Alcohols. Mercuric sulfate (1-1.2 g) and concentrated sulfuric acid (0.75-1 ml) were added to a mixture of 0.1 mole of the 2-cyanoethyl ether of the acetylenic alcohol [3, 4], 10-15 ml of water, and a sufficient amount (80-150 ml) of dioxane to make a homogeneous solution. The mixture was boiled with vigorous stirring for 6-10 hours with addition of 0.75-1 g of mercuric sulfate every 2-3 hours. The sulfuric acid was neutralized with potassium carbonate, the dioxane solution was diluted with ether, the aqueous layer was separated, and the organic layer was dried with sodium sulfate and fractionated. The properties of the 2-cyanoethyl ethers (I) obtained are given in Table 1.

In all cases part of the original 2-cyanoethyl ether was recovered unchanged.

Alcoholysis of 2-Cyanoethyl Ethers (I). The 2-cyanoethyl ether (I) (0.1 mole) was added to 100-150 ml of

methanol containing 15-25 g of dry hydrogen chloride. The mixture was stirred carefully, and the flask was then closed with a stopper carrying a calcium chloride tube and left for two days at room temperature. Methanol was

TABLE 1

$$\begin{array}{c}
 \text{OCH}_2\text{CH}_2\text{CN} \\
 | \\
 \text{R} \diagup \text{C} \diagdown \text{COCH}_3 \\
 \text{R}'
 \end{array}$$

R	R'	Yield (%)	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR		N found (%)	N calc. (%)
						found	calc.		
H	C ₂ H ₅	90	143—146 (16)	1,4324	0,9873	40,75	40,61	*	*
H	n-C ₃ H ₇	86	95—97 (1)	1,4417	0,9863	45,40	45,23	7,97 7,85	8,28
CH ₃	C ₂ H ₅	73	85—87 (1)	1,4381	0,9831	45,14	45,23	8,28 8,28	8,28
CH ₃	n-C ₃ H ₇	62	96—98 (1)	1,4403	0,9810	49,20	49,85	7,37 7,50	7,65
(CH ₃) ₄		79	116—117 (1)	1,4662	1,0580	47,40	47,65	7,72 7,65	7,74
(CH ₃) ₃		50	126—128 (1)	1,4717	1,0506	52,19	52,27	7,35 7,39	7,18

* Found %: C 61.81; 61.60; H 8.65; 8.46. C₈H₁₃NO₂. Calculated %: C 61.93; H 8.39.

distilled off under reduced pressure at a bath temperature of 20-25°, 100-200 ml of water was added to the residue, and the mixture was stirred carefully. The product was extracted with ether, and the ethereal solution was washed with sodium bicarbonate solution and with water, dried with sodium sulfate, and fractionated. The properties of the resulting 2-(methoxycarbonyl)ethyl ethers (II) and (III) are given in Table 2.

TABLE 2

R	R'	Yield (%)	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR		Found (%)		Calculated (%)	
						found	calc.	C	H	C	H
H	C ₂ H ₅ *	21	127—129 (19)	1,4319	1,0296	47,35	47,02	61,81 61,60	8,65 8,46	61,93	8,39
H	n-C ₃ H ₇ *	19	123—125 (11)	1,4338	1,0250	51,30	51,69	59,12 59,30	8,85 8,77	59,40	8,91
CH ₃	CH ₃	75	104—105 (10)	1,4307	1,0388	46,85	47,07	57,20 57,20	8,61 8,45	57,44	8,51
CH ₃	C ₂ H ₅	75	112—114 (10)	1,4342	1,0272	51,44	51,69	59,08 59,30	9,00 8,98	59,40	8,91
CH ₃	n-C ₃ H ₇	10	122—124 (10)	1,4357	1,0122	56,06	56,31	60,92 60,89	9,26 9,28	61,11	9,26
(CH ₃) ₄		60	132—134 (9)	1,4565	1,0809	53,87	54,11	61,61 61,67	8,44 8,43	61,20	8,41
(CH ₃) ₃		86	142—144 (9)	1,4625	1,0659	58,86	58,82	63,63 63,21	8,81 8,82	63,16	8,77

* The mixture was left at room temperature for 20 hours.

SUMMARY

1. The hydration of 2-cyanoethyl ethers of various acetylenic alcohols was carried out.
2. The resulting 2-cyanoethyl ethers of α -hydroxy ketones were converted into the corresponding 2-(methoxycarbonyl)ethyl ethers.

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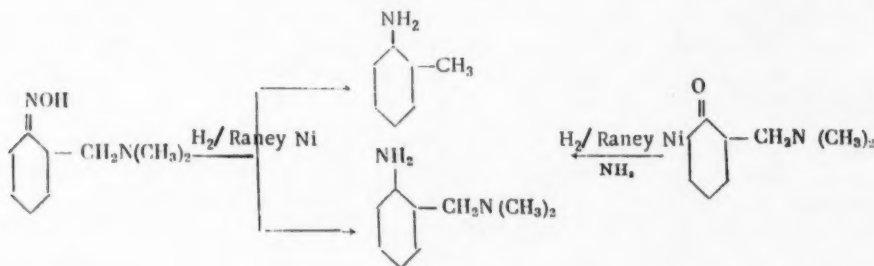
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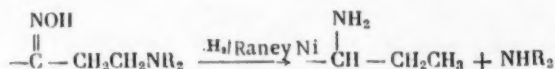
SYNTHESIS OF CYCLIC γ -DIMAINES

I. N. Nazarov and N. V. Kuznetsov

In the development of methods of synthesizing dienes having a fixed transoid system of bonds, such as 3-methyl- γ -cyclohexene, we were faced with the necessity of preparing cyclic γ -diamines, which were not readily accessible. It appeared that it would be possible to prepare cyclic diamines either by the reduction of oximes of β -amino ketones or by reductive amination of the β -amino ketones themselves, which are fairly readily prepared by the Mannich method [1, 2]:



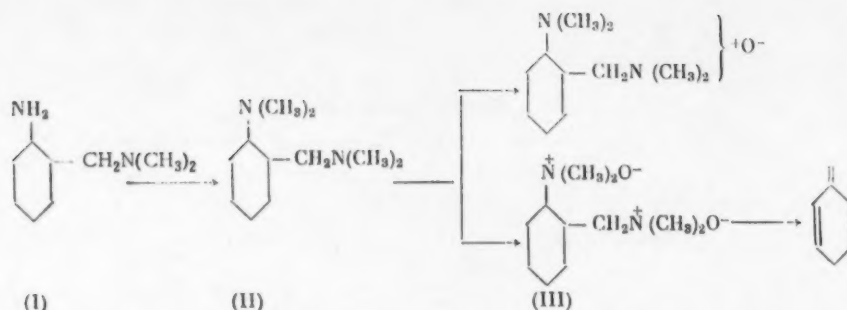
Several cases of the catalytic hydrogenation of oximes of β -amino ketones have been described [3-5], but the reaction is accompanied by hydrogenolysis of the molecule with elimination of an amine:



and no γ -diamines have been prepared in this way. The reduction of oximes of β -amino ketones with sodium amalgam [6] or sodium and alcohol [4] gives γ -diamines in very low yield (less than 30%). All these considerations apply also to the preparation of γ -diamines by the reductive amination of β -amino ketones: either γ -diamines are not obtained at all, or they are obtained in very low yields [7]. Hence, no convenient methods for the synthesis of γ -diamines have been described.

It was shown that the hydrogenation of oximes must be carried out in a small amount of methanol saturated with ammonia in presence of a large amount of Raney nickel at temperatures not above 40°. Hydrogenation of the oxime of 2-(dimethylaminomethyl)cyclohexanone [8] under these conditions gives 2-(dimethylaminomethyl)cyclohexylamine in about 70% yield, and the oxime of 2-(dimethylaminomethyl)cyclopentanone gives the corresponding diamine in 50% yield. The diamines obtained were methylated with formaldehyde and formic acid to give bis-dimethylamino compounds [8].

The bisdimethylamino compound (II) was oxidized with 30% hydrogen peroxide, and a mono- or di-oxide (III) was formed according to the amount of hydrogen peroxide added:



The dioxides were isolated in the form of their picrates. When the dioxide (III) was heated to 100–120° under reduced pressure (20 mm), it was converted into 3-methylenecyclohexene in a yield of about 50%. We studied also the reductive amination of 2-(dimethylaminomethyl)cyclohexanone. It was found that in aqueous ammonia the yield of 2-(dimethylamino)cyclohexylamine (I) was about 65%.

EXPERIMENTAL

Oxime of 2-(Dimethylaminomethyl)cyclopentanone. A mixture of 170 g of cyclopentanone, 82 g of dimethylamine hydrochloride, and 100 ml of 35% formaldehyde solution was boiled for ten minutes and then cooled with ice water. After treatment with water as in the case of the reaction with cyclohexanone [8], we obtained 75 g of unchanged ketone, m.p. 125–130°, and 130 g of the oxime of 2-(dimethylaminomethyl)cyclopentanone. After recrystallization from methanol the substance had m.p. 177–178°. The literature [9] gives m.p. 184°.

Hydrogenation of the Oxime of 2-(Dimethylaminomethyl)cyclopentanone. The oxime of 2-(dimethylaminomethyl)cyclopentanone (31.2 g) was hydrogenated in 30 ml of methanol saturated with ammonia in presence of 8 g of Raney nickel. The reaction was carried out at 40°, and the initial hydrogen pressure was 120 atm. The product, amounting to 13 g (46.5%) was 2-(dimethylaminomethyl)cyclopentylamine, b.p. 92–94° (15 mm); n_D^{20} 1.4830.

Methylation of 2-(Dimethylaminomethyl)cyclopentylamine. A mixture of 8 g of the amine, 15 ml of 35% formaldehyde solution, and 30 ml of 85% formic acid was heated at 100° for 16 hours [8]. The product, amounting to 8 g, was 2-(dimethylaminomethyl)-N,N-dimethylcyclopentylamine, b.p. 106–108° (15 mm); n_D^{20} 1.4895.

Hydrogenation of the Oxime of 2-(Dimethylaminomethyl)cyclohexanone. 1) Hydrogenation of 50 g of the oxime [3] (m.p. 111–112°) was carried out as a solution in 50 ml of methanol saturated with ammonia in presence of 20 g of Raney nickel; an autoclave was used. The reaction temperature was 45°, the initial hydrogen pressure was 130 atm, and the reaction was continued for four hours. The product, amounting to 30 g, was the substance (I), b.p. 112–113° (30 mm) and n_D^{20} 1.4780; its dipicrate had m.p. 216–217° (with decomposition).

2) The oxime (170 g; m.p. 111–112°) was hydrogenated in 500 ml of methanol saturated with ammonia in presence of 15 g of Raney nickel at an initial hydrogen pressure of 100 atm and a reaction temperature of 70–80°. The products were 67 g of 2-methylcyclohexylamine, b.p. 56–61° (15 mm), and 37 g of (I), b.p. 101–103° (15 mm).

Reductive Amination of 2-(Dimethylaminomethyl)cyclohexanone Hydrochloride. 1) Hydrogenation of 20 g of the hydrochloride of the Mannich base (prepared according to [1]) in 100 ml of saturated alcoholic ammonia in presence of 10 g of Raney nickel at 60° and an initial hydrogen pressure of 100 atm gave 3 g (16.7%) of (I), b.p. 104–106° (20 mm) and n_D^{20} 1.4780.

2) Hydrogenation of 20 g of the hydrochloride of the Mannich base in 60 ml of saturated aqueous ammonia in presence of 20 g of Raney nickel at 40° and an initial hydrogen pressure of 100 atm gave 10 g (65%) of (I), b.p. 103–105° (20 mm), and n_D^{20} 1.4775.

Oxidation of 2-(Dimethylaminomethyl)-N,N-dimethylcyclohexylamine with Hydrogen Peroxide. a) With stirring and cooling 7.5 g of 30% hydrogen peroxide was added to 5 g of the substance (II) (which was prepared previously [8]) in 10 ml of methanol; the hydrogen peroxide partially decomposed with evolution of oxygen, and after 30 minutes a further 15 g of 30% hydrogen peroxide was added. After 24 hours the excess of hydrogen

peroxide was decomposed by stirring the mixture with a little platinum black. After being recrystallized from ethanol, the dipicrate of the monoxide of (II) had m.p. 83-85° (with decomposition).

b) To 5 g of the same diamine in 10 ml of methanol we added 7.5 ml of 30% hydrogen peroxide. The addition was repeated six times more at intervals of 30 seconds with stirring and cooling with ice water. After one day the excess of hydrogen peroxide was removed by shaking the mixture with platinum black. The dipicrate of (III) was crystallized from ethanol; it melted at 112-115° (with decomposition).

Pyrolysis of the Diamine Dioxide (III). The above experiment (b) was repeated, and a solution of the combined reaction products from the two experiments was evaporated down at a residual pressure of 10 mm and a temperature of less than 45°. The residue was decomposed by heating it to 100° at a residual pressure of 20 mm, and the reaction products were condensed in a trap cooled with a mixture of solid carbon dioxide and acetone. The usual treatment gave 1.5 g of 3-methylenecyclohexene, b.p. 108-112°; n_D^{20} 1.4920; λ_{\max} 231 m μ ; ϵ 8250 (heptane).

SUMMARY

1. A method was developed for the preparation of γ -diamines by the reductive amination of Mannich bases and also by the reduction of their oximes.
2. It was shown that the dioxide (III) is readily converted into 3-methylenecyclohexene.

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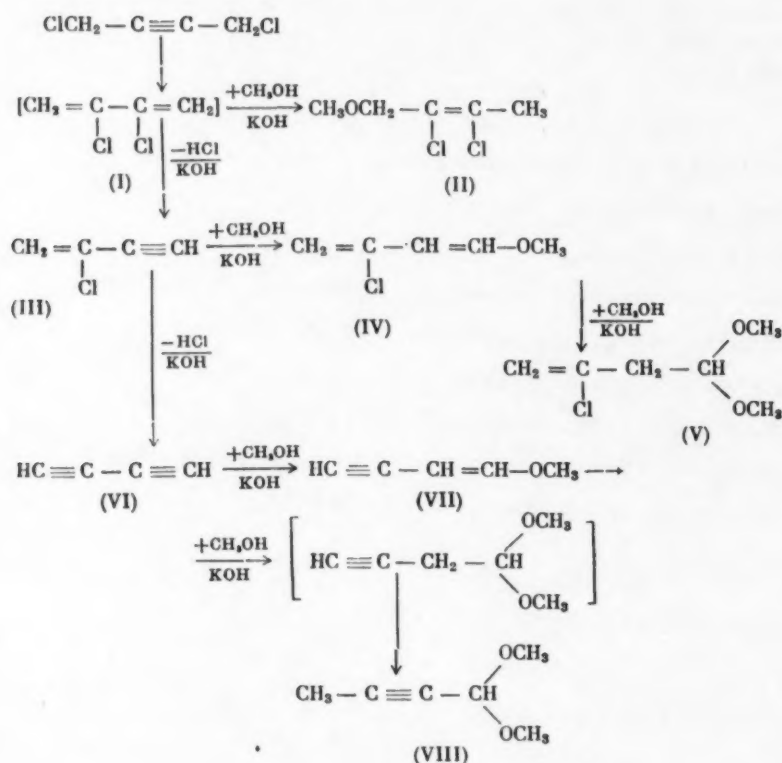
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*Original Russian pagination. See C. B. Translation.

LETTERS TO THE EDITOR

The formation of butadiyne by the action of alcoholic alkali on 1,4-dichloro-2-butyne was established long ago, but the mechanism of this reaction has still not been elucidated. We found that 1,4-dichloro-2-butyne, when treated with methanolic potassium hydroxide, reacts in the isomeric form 2,3-dichloro-1,3-butadiene (I) and forms various products according to the reaction conditions. We obtained the following: 2,3-dichloro-1-methoxy-2-butene (II), b.p. 50° (5 mm); d_4^{20} 1.2090; n_D^{20} 1.4910; 2-chloro-1-buten-3-yne (III), b.p. 63-65° (760 mm); d_4^{20} 1.030 and n_D^{20} 1.4720; 3-chloro-1-methoxy-1,3-butadiene (IV), b.p. 50° (8 mm); d_4^{20} 1.2179; n_D^{20} 1.4680; 2-chloro-4,4-dimethoxy-1-butene (V), b.p. 66° (22 mm); d_4^{20} 1.0262; n_D^{20} 1.4535; butadiyne, m.p. -36° and b.p. 10°; 1-methoxy-1-buten-3-yne (VII), b.p. 50° (50 mm); d_4^{20} 1.9113; n_D^{20} 1.4770 and also b.p. 56° (50 mm) d_4^{20} 0.8987; n_D^{20} 1.4820 and 1,1-dimethoxy-2-butyne (VIII), b.p. 52-53° (12 mm); d_4^{20} 0.9577 and n_D^{20} 1.4359.



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In [1] we gave an approximate equation for isotherms of unimolecular adsorption in presence of adsorbate-adsorbate interactions, and this equation describes convex, concave, and also S-shaped isotherms:

$$h = \theta' / K_1' (1 - \theta') (1 + K_n \theta'), \quad (1)$$

in which h is the relative vapor pressure, θ' is the surface coverage, and K_1' and K_n are adsorbate-adsorbent and adsorbate-adsorbate equilibrium constants. In [1] for multimolecular adsorption we obtained equations that were valid only for particular cases: high K_1' with low K_n and low K_1' with high K_n . We now examine the general case of multimolecular adsorption for any values of K_1' and K_n , taking account of the fact that in the equilibrium equation for primary adsorbate-adsorbent interaction

$$K_1' = \theta_{01}' / h (1 - \theta') \quad (2)$$

there enters a concentration of only θ_{01}' uncovered single complexes of the first layer. For at any given value of h $\theta_{01}' / \theta_1' = \theta_{02}' / \theta_2' = \dots = \theta_0' / \theta'$, in which θ_{01}' , θ_{02}' , \dots and θ_1' , θ_2' refer, respectively, only to uncovered and to all single, double, etc. horizontal complexes of the first layer and θ_0' and θ' , respectively, to all uncovered and to all complexes of the first layer. Let us assume that adsorbate-adsorbate interaction in the first layer does not depend on whether the horizontal complexes of this layer carry vertical complexes or not. According to (1) $\theta_1' = \theta' / (1 + K_n \theta')$, and the total coverage is $\theta = \theta_0' / (1 - h)^2 = \theta' / (1 - h)$. Introducing θ_{01}' , θ_1' , θ_0' and θ' into (2), we obtain an equation for the isotherm of multimolecular adsorption of vapor which takes account of adsorbate-adsorbate interaction in the first layer:

$$h = \frac{\theta (1 - h)^2}{K_1' [1 - \theta (1 - h)] [1 + K_n \theta (1 - h)]} \quad (3)$$

When $K_n = 0$ this equation passes into the BET equation, just as Equation (1) passes into the Langmuir equation [1].

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CURRENT EVENTS

JUBILEE SESSION OF THE DIVISION OF CHEMICAL SCIENCES OF THE ACADEMY OF SCIENCES OF THE USSR, OCTOBER 30-31, 1957, AND GENERAL MEETING OF THE DIVISION OF CHEMICAL SCIENCES, DECEMBER 19-20, 1957

In celebration of the fortieth anniversary of the Great October Socialist Revolution, the Division of Chemical Sciences of the Academy of Sciences of the USSR held a Jubilee Session on October 30 and 31, 1957. In his introductory address, the Academician-Secretary of the Division of Chemical Sciences, Academician N. N. Semenov, spoke of the outstanding progress made in the Soviet Union in the development of science and technology in the course of forty years, culminating in the realization of the people's greatest dream, the creation of an artificial earth satellite. In discussing achievements in chemistry and chemical technology, Semenov emphasized the progress in the Soviet Union of such important branches of chemistry as kinetics, catalysis, photochemistry, electrochemistry, and the chemistry of heteroorganic compounds; attention was drawn also to various lines of work in organic, inorganic, and colloid chemistry which have been developed with brilliant success by the work of Soviet scientists. In conclusion, Semenov named some new directions along which Soviet chemistry should develop, while proceeding further along the old.

Scientific communications, most of which have already been published, were read by the following. Academician I. L. Kurniants, and A. V. Fokin (Nitration of Fluoro Olefins [1]). Academician of Acad. Sci. Arm. SSR A. L. Mndzhoian, whose paper (Investigations on the Synthesis of Physiologically Active Compounds) concerned important investigations on the synthesis of amino esters of various series; these revealed regularities that provided a theoretical basis for the synthesis of cholinolytics and made it possible to develop some valuable new medicinals and introduce them into medical practice. Dr. Chem. R. Kh. Freidlina (Investigation of Telomerization and of Synthesis Based on Telomers [2]). Dr. Chem. B. A. Dolgoplosk (Generation of Free Radicals in Solutions and their Reactions in Model Systems [3]). Academician A. N. Frumkin (Some General Questions of Electrochemical Kinetics and the Theory of Ionic Reactions [4]). Dr. Chem. A. V. Kiselev (Some Problems of the Theory of Adsorption [5]). Dr. Chem. N. M. Emanuel (New Problems in the Field of Chain Reactions [6]). Cand. Chem. V. L. Tal'roze, who reported investigations on the mass spectroscopy of ionic and free-radical reactions. Academician A. P. Rebinder, who reviewed the development of physicochemical mechanics [7]. Corr. Member Acad. Sci. USSR I. V. Tananaev, who reported new results on the chemistry of some rare elements [8]. Dr. Chem. D. I. Riabchikov (co-authors M. M. Senfavin and Yu. S. Skliarenko), who read a paper on aspects of the chemistry of the rare-earth elements. Dr. Chem. V. A. Sokolov, who gave the concluding address on calorimetric measurements at high temperatures.

* *

A general meeting of the Division was held on December 19 and 20, 1957. Members of the Bureau of the Division, Academician S. I. Vol'fkovich and Corr. Member Acad. Sci. USSR M. M. Shemiakin, acted as chairmen. A paper entitled "Study of some Reactions of Peroxy Acids and Hydrogen Peroxide by the Isotope Method" was read by Corr. Member Acad. Sci. USSR A. I. Brodskii (co-authors I. F. Franchuk and V. A. Lunenok). The heavy oxygen isotope O^{18} , introduced into water or a salt, was applied in the study of the mechanism of the anodic formation of salts of some peroxy acids and of their hydrolysis, and also in some oxidation reactions of hydrogen peroxide.

By the method of isotopic dilution it was shown that the hypothesis of the primary intermediate formation of hydrogen peroxide in the anodic preparation of persulfate is incorrect. It was shown also that in the electrolysis of $KHSO_4 + H_2O_2$ solutions the formation of persulfate and the discharge of H_2O_2 are two parallel and independent anode processes.

In the electrolytic preparation of perborate in the usual way from $\text{Na}_2\text{CO}_3 + \text{Na}_2\text{B}_4\text{O}_7$, percarbonate is first formed at the anode, and this then gives its peroxy group to the borate with formation of perborate. The perborate formed under these conditions is a molecular compound of borate and H_2O_2 , and not a true peroxy acid. In the hydrolysis of persulfate, perborate, percarbonate, and perphosphate in H_2O^{18} , the hydrogen peroxide formed is free from excess of O^{18} , so that the oxygen of water plays no part in its formation and the peroxy group from the salt of the peroxy acid passes unchanged into the hydrogen peroxide. In the thermal decomposition of a solution of perphosphate in H_2O^{18} , the extent to which the oxygen of water contributes to the O_2 liberated depends on the pH of the medium. In acid solutions all the O_2 comes from the salt. At pH 4-10, the proportion of the oxygen arising from the water increases linearly with pH, and in alkaline solutions all of the O_2 is derived from the oxygen of the water. These relationships are similar to those found previously by Kolthoff and Miller for persulfate, but they are not in accord with the mechanism proposed by these authors.

Corr. Member I. A. Kazarnovskii, Corr. Member A. A. Grinberg, Academician A. N. Frumkin, and Corr. Member S. Z. Roginskii contributed to the discussion.

A paper on "The Application of N^{15} in the Elucidation of the Mechanism of Some Organic Reactions" was read by Corr. Member Acad. Sci. USSR M. M. Shemiakin. He stated that it is possible to solve various important problems of organic chemistry with the aid of N^{15} . Thus, a new method was proposed for the study of the dual reactivity of compounds with the aid of labeled compounds. In some cases the method can give a unequivocal answer to the question of whether the dual reactivity is the result of tautomerism or of transfer of reaction center. The new method affords the possibility of studying dual reactivity in various symmetrical systems. In particular, with the aid of the new method the existence of diazoamino compounds in two tautomeric forms was proved for the first time, and it was established that their dual reactivity is not associated with transfer of reaction center in the course of the reaction. He used N^{15} also in the study of the formation of osazones. With the aid of labeled arylhydrazine $\text{ArNHN}^{15}\text{H}_2$ he showed that this reaction occurs not in accordance with the well-known scheme of E. Fischer, but in accordance with one of the schemes later proposed by F. Weygand, i.e., via an intermediate compound of the type $\text{RCOC}(\text{NH})\text{R}$. The speaker stated that the reaction proceeds according to this scheme irrespective of the character of the original hydroxy carbonyl compound (the investigation was carried out with the hydrazones of fructose, benzoin, and hydroxycyclohexanone).

M. M. Shemiakin showed that N^{15} has been found extremely useful in the elucidation of the mechanism of formation of azoxy compounds and of some of their reactions. By the use of labeled nitrosobenzene $\text{C}_6\text{H}_5\text{N}^{15}\text{O}$ as starting material it was proved experimentally for the first time that the azoxy-coupling reaction proceeds through the intermediate formation of the dihydroxy compound $\text{ArN}(\text{OH})\text{N}(\text{OH})\text{Ar}$. On the other hand, the synthesis of labeled azoxybenzene $\text{C}_6\text{H}_5\text{NO} = \text{N}^{15}\text{C}_6\text{H}_5$ opened up the possibility of studying the isomerization of azoxy compounds (Wallach rearrangement and allied reactions). It was discovered that in several cases the first stage in these transformations is the formation of symmetrical epoxides $\text{ArN} \begin{array}{c} \diagup \diagdown \\ \text{O} \end{array} \text{NAr}$.

Corr. Member D. N. Kursanov, Corr. Member Ia. K. Syrkin, and Corr. Member M. I. Kabachnik took part in the discussion.

In a paper entitled "Investigation of Electrophilic and Homolytic Substitution Reactions at a Carbon Atom by the Isotope-Exchange Method" Dr. Chem. O. A. Reutov stated that symmetrical aromatic organomercury compounds react in an unexpected way with mercury under very mild conditions:



The rate of reaction is greatly dependent on the character of X; it increases in the order: $\text{O}_2\text{N}, \text{Cl} < \text{H} < \text{CH}_3 < \text{OCH}_3$.

In the case of bisnitrophenylmercury and bischlorophenylmercury, isotopic equilibrium is established in pyridine at 60° in the course of 25 hours, but in the case of bismethoxyphenylmercury in the course of 3 hours. Bismethoxyphenylmercury reacts fairly quickly with mercury, even in the cold. It is probable that direct reaction occurs between diarylmercury molecules and the mercury. In a study of the reaction of aliphatic and alicyclic organomercury salts with mercury it was found that under mild conditions (in the cold in benzene solution) only α -mercurated carbonyl compounds react. The speaker has shown that the reactivity rises in the following order:

propyl (chloromercuri)acetate < 3-(bromomercuri)camphor < 3-benzyl-3-(bromomercuri)camphor < 1-menthyl (bromomercuri)phenylacetate < ethyl (bromomercuri)phenylacetate < 2-(bromomercuri)cyclohexanone. 1-(Chloromercuri)camphenilone, 2-(bromomercuri)camphane, butylmercury bromide, and sec. butylmercury bromide do not react with mercury even at 80°.

Isotopic exchange of organomercury salts of the α -mercurated carbonyl compound type with HgX_2 also proceeds under fairly mild conditions in benzene, dioxane, or acetone solution at 23-50°. The reactivity rises in the order: 3-(bromomercuri)camphor < 1-menthyl (bromomercuri)phenylacetate < ethyl (bromomercuri)phenylacetate < 3-benzyl-3-(bromomercuri)camphor and 2-(bromomercuri)cyclohexanone. 1-(Chloromercuri)camphenilone, 2-(bromomercuri)camphane, butylmercury bromide, sec. butylmercury bromide, and cis- and trans-(2-methoxycyclohexyl)mercury chlorides did not react with mercuric halide under these conditions.

It is probable that isotopic exchange of the cited organomercury salts with mercuric halide is an electrophilic-substitution reaction at a saturated carbon atom. Substitution at an olefinic carbon atom was studied for the case of chlorovinylmercury compounds. The reactions of cis- and trans-(2-chlorovinyl)mercury chlorides both with Hg and with HgCl_2 , and also of cis- and trans-bis-2-chlorovinylmercurys with Hg , proceed with strict preservation of the configuration. It was shown by special experiments that (2-chlorovinyl)mercury chlorides react directly with Hg and HgCl_2 , and not through the stage of equilibrium with bis-2-chlorovinylmercury and mercuric chloride.

Corr. Member B. V. Nekrasov, Corr. Member S. Z. Roginskii, and Corr. Member Ia. K. Syrkin took part in the discussion.

Corr. Member Acad. Sci. USSR I. P. Alimarin reported on new methods for the determination and separation of rare elements by the use of organic derivatives of sulfurous, selenous, and tellurous acids. The speaker stated that organic reagents containing the AsO_3H_2 , PO_3H_2 , and SO_2H groups are of great interest from the analytical point of view, as has been shown by the work of Feigl, Thomas, Dubskii, Krishna, Kuznetsov, Alimarin, and others, but organic compounds containing the SeO_2H and TeO_2H groups have not yet been studied with a view to their use in quantitative analysis.

The speaker has synthesized and investigated for the first time organic derivatives of sulfurous and selenous acids: methane-, ethane-, propane-, butane-, benzene-, and naphthalene-seleninic acids, and also o-nitro-, p-nitro-, o-carboxy-, and p-methyl-benzeneseleninic acids. He also studied the analytical properties of benzene-seleninic and benzenesulfonic acids and of acid phenyl esters of tellurous, selenous, and telluric acids. The effect of the nature of the substituent (NO_2 , COOH , CH_3 , and $=\text{CH}_2$) and of its position in the aromatic nucleus on the solubility of the salt was determined; in this, use was made of the radioactive isotopes iron-59 and zirconium-95. It was shown that the solubility is related to the change in electron density in the benzene nucleus and to the "weighting effect." A study was made also of the effect of pH and of complex-formers on the selectivity of ammonium benzene- and naphthalene-seleninates.

I. P. Alimarin investigated the behavior of benzenesulfonic, benzeneseleninic, and benzenetellurinic acids toward oxidizing and reducing agents and showed that the ability of benzeneseleninic acid to be reduced by potassium iodide to diphenyl diselenide can be applied successfully in the volumetric iodometric determination of several elements.

New gravimetric methods in which ammonium benzene- and naphthalene-seleninates are used have been developed by the author for the determination of titanium, cerium, bismuth, and iron in the presence of other elements. The method of isotopic dilution was applied in the determination of niobium, tantalum, and some other quadrivalent elements. Also, potentiometric and amperometric methods were developed for the determination of several elements, including bismuth, and also gravimetric methods were devised for the determination of thorium and zirconium in presence of other elements with the aid of benzenesulfonic acid.

Dr. Chem. V. I. Kuznetsov took part in the discussion.

Dr. Chem. V. G. Levich read a paper entitled "Diffusion Kinetics of Heterogeneous Reactions in Moving Liquids." The speaker stated that the development of quantitative methods for the study of the kinetics of heterogeneous reactions made the qualitative concepts developed by Nernst and Langmuir inadequate.

* Radioactive mercury isotope Hg^{203} .

In several cases encountered in practice, particularly in electrochemistry and chemical technology, the diffusion stage determines the over-all rate of a heterogeneous reaction. The creation of a quantitative theory of the diffusion stage of heterogeneous reactions has therefore become urgent. Heterogeneous reactions generally occur in moving media. A general theory of convective diffusion, as it occurs in liquids, was developed. The low magnitude of diffusion coefficients in liquids made it possible to find general methods of solving convective-diffusion equations and to apply them in the solution of actual problems. The quantitative values found for the rates of the diffusion stages of heterogeneous reactions for the different interfaces (solid-liquid, liquid-liquid, and liquid-gas), the geometric conditions, and the hydrodynamic states of liquid movement (laminar, turbulent) were subjected to experimental verification in numerous investigations in the Soviet Union and abroad.

The close agreement observed between theory and experiment enabled the author to proceed with confidence in the application of the theoretical expressions found to the analysis of heterogeneous reactions (determination of the order of reaction, the reaction kinetics, etc.), to develop analytical methods that compete successfully with polarographic methods (rotating disc electrode), and also to obtain the theoretical values of the rates of elementary acts of various processes of chemical technology.

The study of the diffusion kinetics for a turbulent state of the liquid, which is very often met in practice, required the development of the modern theory of turbulence and, in particular, the determination of the spectrum of turbulent pulsations near solid-liquid interfaces. The speaker reported the development of new methods of studying turbulence near interfaces and in small-scale systems; these are based on physicochemical measurements and also on an examination of questions of diffusion kinetics in presence of an electric field and space charges.

Drs. Chem. N. A. Bakh, I. L. Rozenfel'd, A. M. Rozen, and I. R. Krichevskii took part in the discussion.

LIST OF PUBLISHED PAPERS READ AT THE JUBILEE SESSION

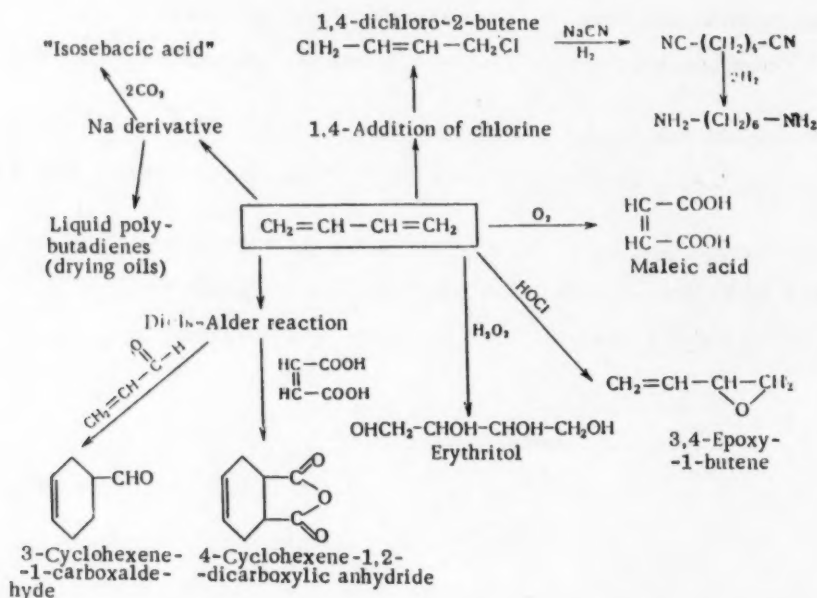
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*Original Russian pagination. See C. B. Translation.

CHEMICAL CONFERENCE IN THE GERMAN FEDERAL REPUBLIC, 1957

The annual meeting of the German Society for the Investigation of Petroleum and the Chemistry of Coal, the president of which is our recent guest Professor K. Ziegler, took place on October 10-12, 1957, in Western Berlin. In all there were four plenary and 27 sectional papers in three sections working simultaneously: a) geology, b) petroleum chemistry, and c) coal chemistry. We were concerned only with the papers on petroleum and coal chemistry.

In a plenary paper F. Zobel (Jules Marle Chemical Combine) reviewed the present state of the petrochemical industry. He discussed various aspects of the chlorination of methane and its homologs. Whereas at 450° in presence of a deficiency of chlorine, methane is chlorinated to methyl chloride, methylene chloride, and chloroform, at 600° in presence of excess of chlorine, carbon tetrachloride is formed; at 600°, in presence of a deficiency of chlorine, tetrachloroethylene is also formed. The chlorination of propane gives 1-chloropropane (b.p. 46.8°) and 2-chloropropane (b.p. 34.8°), which are readily separated by fractional distillation. The further chlorination of 1-chloropropane gives 1,2- and 1,3-dichloropropanes, and the chlorination of 2-chloropropane gives 2,2-dichloropropane. He further stated that the yields of butadiene attained in the catalytic dehydrogenation of 1-butene are 26.2% at 0.1 atm and 43.5% at 0.01 atm.



Oils for aviation, of low freezing point and high stability to oxidation, are obtained either by the esterification of sebacic acid with 1,2-propanediol or by the esterification of "isosebacic acid" (synthesized from butadiene) with ethylene glycol. As will be seen from the following scheme, butadiene, apart from being used in the manufacture of synthetic rubber, is becoming an important raw material in various fields of industrial organic synthesis.

In another plenary paper Prof. A. Bentz (President of Well-sinking Department, Hanover) reviewed the possibilities of discovering new sources of petroleum in various countries (apart from the USSR). He pointed out that in the coming decade a colossal amount of energy of all kinds would be required and, on the basis of various calculations, the existing reserves of energy are quite inadequate to maintain the energy balance. As regards nuclear energy, it is still not clear when and on what scale it will be able to satisfy the enormous demands of industry. It is therefore necessary to analyze the actual possibilities of increasing the world production of petroleum. After reviewing the notable new discoveries of petroleum in the Near East, the speaker urged that account should be taken of the prospects in other parts of the world. Thus, in Europe, in which, according to international statistics, there were only extremely small oil fields until recently, successful investigations and prospecting had now resulted in the appearance of new sources of petroleum in France, the Netherlands, Italy, Austria, and Germany which provide an annual production of more than 15 million tons. Prognosis with the aid of the oil chart compiled at the Well-sinking Department, Hanover, suggests that in these areas there are still many unexplored possibilities.

Until now Africa has yielded an extremely minute amount of petroleum. However, vigorous prospecting in French Equatorial Africa, Angola, the Cameroons, and particularly the Sahara has led to discoveries that make it necessary to re-examine the distribution of oil reserves, for the potentialities of the Sahara are comparable to those of the Near East. On the American continent, particularly in Canada and in the foothills of the Andes, there are districts having characteristics that give hope for the discovery of considerable oil deposits. In Asia, mainly in the geologically investigated districts in India, several large petroleum-producing areas have been found.

On the basis of this review the speaker concluded that, though it is now usual to consider that two-thirds of the world reserves of petroleum is concentrated in the Near East, in the future this picture will very probably suffer substantial changes.

One of the plenary papers was presented by H. Hoffmann (Daimler-Benz Co., Stuttgart), who discussed "Fuel and the Engine." The author reported the results of investigations on the matching of the fuel to the engine in the case of engines of recent development, mainly Diesel engines and engines working with an Otto cycle. New data have been obtained on the flammability of fuels of high aromatic content and high octane rating. Such fuels were found to be not very sensitive to detonation in antechamber compression-ignition engines. On the other hand, a close correspondence was found between the flammabilities of various fuels in engines of this type and their anti-knock values in Otto engines. It has recently become standard practice in the U.S. to use fuels of octane rating 98 in automobile engines; this permits the use of compression ratios of 10 or more. At the same time engine designers have found that such compression ratios can be obtained not only by the use of fuel of high antiknock value, but also by the selection of the most favorable form of the combustion chamber, which results also in a considerable economy of fuel. This was proved with American V-8 engines. On the basis of the experimental data it was shown that a fuel of not very high octane rating may be used in German automobile engines while utilizing not only very high compression ratios, but also the maximum moment of rotation, i.e., a high acceleration rating. In conclusion the speaker stated that at present the fuel characteristics required for the Otto engine could not be regarded as completely established, and further investigation was necessary.

Interesting sectional papers were presented by A. Hoppe (Frankfurt) (Heid Paraffin-separation Plant); M. Freund (Budapest) (Chemical Changes of Hydrocarbons in a High-tension Field as an Analogy of Radiochemical Changes); H. Koelbel (Berlin) (Synthesis of Hydrocarbons from Carbon Monoxide and Water over Cobalt or Ruthenium Catalysts); I. Freving (London) (Lubricant Problems at Nuclear Power Stations); O. Joclin (Lugano) (Preparation of Dicarboxylic Acids from Raw Material other than Naphthalene); L. Wiesner (Hanover) (Significance of Nuclear Radiations in the Processing of Petroleum and Coal); L. Rappen (Duisburg-Meiderich) (New Method for the Quantitative Determination of the Main Components of Technical Mixtures of Phenols).

According to Prof. Koelbel, the synthesis of liquid hydrocarbons over a cobalt catalyst is accompanied by negligible methane formation, the yield of liquid products attains 98-99%, and the yield of C_3 and higher hydrocarbons attains 200 g per cu.m of carbon monoxide. The author gave numerous experimental data on the effect of temperature, composition of the gas phase, space velocity, pressure, etc. on the life of the catalyst and the extent of side reactions. At atmospheric pressure ruthenium gives a high yield of liquid hydrocarbons, but at a pressure of about 100 atm high-melting paraffins are formed in almost quantitative yield. For liquid-phase reaction the catalyst can be used as a suspension in water; which in this case acts simultaneously as carrier and reactant.

In papers on nuclear radiations it was pointed out that both electrons and also x- and γ -rays cause the ionization of the molecule with resulting cleavage of chemical bonds and formation of radicals. Unlike paraffins, aromatic

hydrocarbons can stand a fairly large amount of radiation energy without appreciable decomposition. Whereas under the action of thermal energy, butane, for example, undergoes mainly degradation reactions, under irradiation it forms mainly synthesis products: octane, octene, and C_{12} , C_{16} , and C_{20} hydrocarbons. Study was made of such irradiation conditions under which hydrocarbons do not change in structure while at the same time harmful impurities (e.g., thiols) are removed. In these papers the view was expressed that the coming of large nuclear power stations is bound to lead to the development of new methods of processing petroleum and coal, but for such development at least ten years of systematic research is necessary.

The new method of determining phenols in technical mixtures described in Dr. Rappen's paper consists in the construction of freezing point diagrams of mixtures of phenol, cresols, xyenols, and 2,3,5-trimethylphenol taken in different proportions. In these diagrams account was taken of possible discrepancies associated with the formation of double compounds, which can invalidate calculations based on Raoult's law. However, these discrepancies are characteristic only of complex high-boiling phenol homologs. This method makes it unnecessary to distill phenol and m-cresol from the mixture to be analyzed, a procedure which generally results in some complications. It does not require intricate apparatus and has the advantage that the analysis can be carried out with a small amount of material.

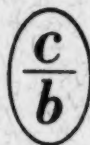
The Soviet delegates at this conference were Corr. Member N. I. Shuikin and Corr. Member A. D. Petrov. We were welcomed not only by the President of the Society, but also by other specialists of the German Federal Republic: Dr. H. Koch (Mülheim); the editor of *Erdöl und Kohle*, Prof. K. Zerbe, who requested that Russian chemists should submit papers to his journal; Prof. H. Koelbel (Technical University, Berlin), and others. At the end of the conference we enjoyed Prof. Koelbel's hospitality and made a detailed inspection of the three-storied building which houses the extensive fuel laboratories of the Technical University. We exchanged reprints and monographs with Professors Koelbel and Zerbe. We took part also in an excursion in West and East Berlin.

A. D. Petrov and N. I. Shuikin

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PROCEEDINGS OF THE FIRST ALL-UNION CONFERENCE ON RADIATION CHEMISTRY, MOSCOW, 1957

THIS UNPRECEDENTED RUSSIAN CONFERENCE on Radiation Chemistry, held under the auspices of the *Division of Chemical Sciences, Academy of Sciences, USSR* and the *Ministry of Chemical Industry*, aroused the interest of scientists the world over. More than 700 of the Soviet Union's foremost authorities in the field participated and, in all, fifty-six reports were read covering the categories indicated by the titles of the individual volumes listed below. Special attention was also given to radiation sources used in radiation-chemical investigations.

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